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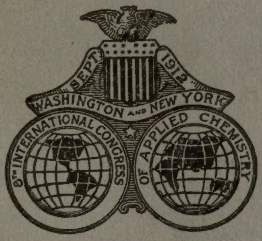
ORIGINAL COMMUNICATIONS

EIGHTH INTERNATIONAL

CONGRESS
OF APPLIED CHEMISTRY

Washington and New York
September 4 to 13, 1912

SECTION Xa: ELECTROCHEMISTRY


SEPT. 1912
WASHINGTON AND NEW YORK
8TH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY

VOL. XXI.

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UNIV. OF
CALIFORNIA

VOL. XXI

TP6
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1918
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THE FUNCTION OF SLAG IN ELECTRIC STEEL REFINING

RICHARD AMBERG
East Orange, N. J.

While the old time melter was satisfied to bring his metal out in the desired condition and therefore took care of having the slag liquid enough, the importance of a thorough knowledge of the slag is at present recognized in all up-to-date melting shops. Formerly, slag or cinder was considered a necessary evil, accumulating in some mysterious way, wherever a man was striving to produce a clean metal. Nowadays we are deliberately aiming at a well defined slag which varies with the nature of processes applied and products wanted.

In steel making we need, in general, slag for two main purposes, i. e.—for refining and for protecting the metal. To refine metal, essentially oxidizing and reducing processes are required, while to protect the metal we need a reducing or, still better, a neutral atmosphere. Although an absolutely neutral condition between steel, on one side, and the containing vessel and the slag, on the other, is an imaginary conception, the various furnaces in use for the production of liquid steel may be arranged with respect to the attainment of this ideal in about the following order of merit: converter; open-hearth; crucible; and electric furnace.

In dealing with our subject we will find it convenient to avail ourselves of the terms of physical chemistry, which yield a simple conception of the matter and an expedient way of expression.

Slag and metal at large are not mixable with each other, and we will therefore call them the two "immiscible phases," though there are certain compounds which dissolve in both phases under conditions to be considered later on. Reactions between chemical compounds can take place in either phase; they are independent of the reaction in the other phase as long as the product of the reaction remains in its own phase and does not cross the boundary surface. A reaction of this kind, where the original and the final product are entirely in one and the same phase, is a homogeneous reaction. If the other phase takes part by either supplying or absorbing substances, the reaction is heterogeneous. The homogeneous reaction is governed by the laws of homogeneous chemical equilibrium or mass action; it occurs uniformly throughout the entire phase.

Since, according to Van't Hoff, at low temperatures an increase of 10°C. doubles the reaction velocity, it will in most cases be infinitely high at the temperatures of the steel bath. The heterogeneous reaction, however, must take place at the contact surface of the two phases. Its speed depends greatly on the velocity with which the substances participating in the reaction are brought to the contact surface, and carried away from it. That is—it depends greatly on diffusion and mechanical convection.

Every condition which makes the slag less viscous and more agitable, facilitates, therefore, a heterogeneous reaction. Further, the greater the area of the contact surface between the two phases, the more is the heterogeneous reaction facilitated.

Some time ago[1] the author pointed out briefly these facts, which are discussed more in detail in the present paper.

The above considerations will hold good for many kinds of metallurgical operations. When applying them to a practical case we have to bear in mind that slag and metal are very seldom separated by a sharp surface: small particles of slag are hanging through the surface of the metal, are cut off and scattered through the bath, and little balls of steel are oftentimes found mixed within the slag. Considering a steel furnace in operation, we have to deal with at least four phases—viz: the slag, and the metal, as the two liquid phases; the atmosphere above the bath; and one or more solids in the hearth of the furnace. The solid phases, however, can be disregarded entirely for the purpose of this paper, while the gas phase will occasionally have to be taken into account.

The function of the slag in an electric steel furnace depends on the kind of work which the furnace is performing; that is, the particular process which is carried out, and in one and the same process the function of the slag depends on the stage which the operation has reached at that time.

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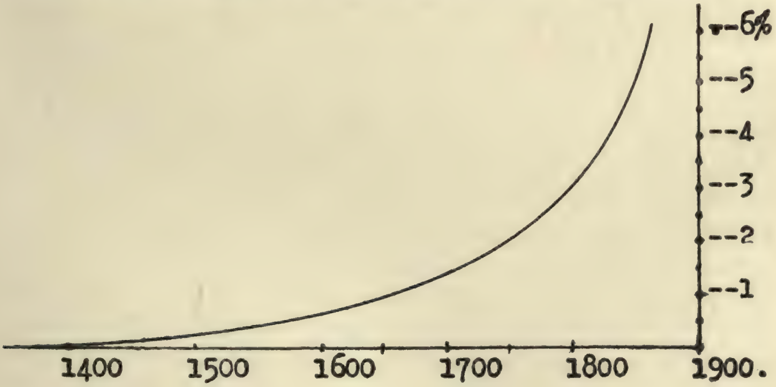
[1] Met. and Chem. Engrg. Vol. 7, 1909, p. 115; also Stahl und Eisen, 1909, Nr. 5.

At places, where cheap power is available, electric steel melting begins with the most widely known open-hearth process by melting pig and scrap. It is also possible to start with steel scrap without any pig iron, although this is not an advisable practice, since it is hard on the lining. Assuming a basic-lined bottom and hearth heated by one or more electric arcs, the charge melts down, slag is formed by lime, silica, and iron-oxide in the form of ore or scale, and the refining by oxidation takes place in form of heterogeneous reactions of different kinds. After the ferric oxide dissolved in the slag has been reduced to ferrous oxide, it partly acts directly on those parts of the metallic solution which come in immediate contact with it, and partly dissolves in the metal according to temperatures and coefficient of division of FeO between the two phases. If the slag is saturated with FeO, the latter can assume its full concentration in the metal bath according to the solubility curve, given 1906, by Prof. Eichoff.



Its action here on manganese and the metalloids is much the same as in the open-hearth, and needs no discussion at this time. It can be more energetic, however, if the operator avails himself of the facility of a higher temperature, which is a special feature of the electric furnace, and as Fig. 1 shows, of a higher concentration of FeO.

There is one essential difference from the reactions in an open-hearth slag. In a well built electric furnace, practically all the oxygen required has to be supplied in solid oxide form, while the open-hearth has an unlimited supply of oxygen by opening its air inlets wide enough to have an excess in its gases, from which the slag continuously and automatically replaces the amounts transferred to the steel. A poorly constructed electric furnace, which the author once saw, produced such a tremendous draft of air through its doors that it almost did not need more ore than an open-hearth furnace.

At this period of oxidation the basic slags of an arc furnace and of an induction furnace show a material difference: the dephosphorization, being a process which reaches its maximum velocity at a temperature somewhat below the melting point of soft iron, is accomplished more quickly in the comparatively colder slag of the induction furnace than under the higher heat of the arc. The technical significance of this fact though, is small at the present time, since the general and indeed reasonable tendency is to do as much of the refining work as possible in the open-hearth furnace and reserve for the electric furnace merely those finishing operations for which it is especially fitted, and which can not be performed in the open-hearth.

In view of the above described conditions, the analysis of the slag during this period does not offer any particular interest in comparison with open-hearth slag. CaO will run in the neighborhood of 40%, sometimes 5 to 8% lower, iron and manganese oxides 26 to 29% together, and the silica will vary with the silicon of the charge, and the additions. P_2O_5 may run up to any amount in crude open-hearth work, yet, as a rule the slags have been skimmed, when it reached something like 4%. As manganese ore, even at this stage, helps desulphurization, it seems to act locally, perhaps near the electrodes only, in a manner which will be discussed later on.

After this oxidation has been carried on far enough, and the slag removed, or after dephosphorized metal has been transferred from another furnace to the electric furnace, (which practice is the rule in the present centers of the steel industry,) the metal will be deoxidized in the furnace. This involves a slag process which none of the other furnaces can perform. Carbon is the chief deoxidizing agent and is bound to act in both phases. Experience has shown that this element alone can complete the deoxidation, but it is not practical commercially to do this, as it takes too long a time. While the action of carbon on oxides in the homogeneous metal phase probably goes on with sufficient velocity, yet its action on the oxides of the slag, being a heterogeneous reaction, is pretty slow. We know that glass can be colored by small quantities of carbon, but we have not found that any amount of carbon worth while could exist as dissolved in the slag phase. Furthermore, when the metal will be freed from the compounds which are soluble in both phases, these compounds will have the tendency to diffuse back from the slag into the metal as soon as favorable chemical and thermal conditions should arise.

Phosphorus may be mentioned as an example for this statement. An iron-phosphide exists in the metallic solution; by oxidation, transfer to the other phase, and neutralization with CaO, it forms calcium-phosphate. When finishing a basic open-hearth heat the amount of oxygen in the slag decreases gradually and can reach a point, where the other sources of oxygen are so much exhausted that the phosphate begins to be reduced by iron or manganese and the phosphorus re-enters the bath—one of the dangers which the skilled melter knows how to avoid. Here the electric heating, as described in the patents of Humbert, offers the possibility to heat the slag with the addition of carbon in a reducing atmosphere so quickly that it forms a considerably higher endothermic compound, probably Ca_3P_2, which is not reabsorbed by the steel phase; hence the opportunity to dephosphorize without skimming the slag. How sensitive this reaction is with respect to temperature, is shown by the fact that without very accurate control of the temperature a rephosphorization of the metal has been found.

Since in the reducing atmosphere, when carried on far enough, the partial pressure of oxygen is very low, the oxygen can be removed to a considerable extent from both phases without disturbing the equilibrium at the contact surface, while the opposite would be the case with an open-hearth furnace. In fact, the amount of FeO present in the final slag is easily brought down in everyday practice to between 1% and 0.5%, and with a little attention, considerably lower. The reaction, by which this is performed, is a true heterogeneous one and consequently does not come to an equilibrium in the original phase: FeO as a base of the silicates or as dissolved in the slag is freed from oxygen and the metal joins the other phase. Manganese is practically removed from the slag in a similar way. Even silicon is partly reduced, when the basicity of the slag and the temperature both are high enough.

The desulphurization has been the subject of many experiments and discussions. No doubt, there are three phases, the atmosphere and the two liquids, connected with this phenomenon. In the oxidizing period, where sulphur is being removed only to a small extent in the open-hearth, the electric furnace is much more efficient in this respect, especially when manganese ore is used. It is likely that a good bit of the sulphur forms SO_2 and disappears with the gases; as the partial pressure of O and of SO_2 in the atmosphere of the electric furnace is smaller than in the open-hearth, the reaction takes place more easily. This is the reason why, as previously mentioned, the electric furnace in all other respects is less good an instrument for oxidizing refinement than the open-hearth.

In the reducing period a new desulphurizing action takes place, which the author formulated some time ago.[1]

(1) $FeS+CaO+C=Fe+CaS+CO$ at high temperatures of the arc furnace.

(2) $2\,CaO+3\,FeS+CaC_2=3\,Fe+3\,CaS+2\,CO$ at still higher temperatures, where the calcium-carbide can be formed.

(3) $2\,FeS+2\,CaO+Si=2\,Fe+2\,CaS=SiO_2$ at the lower slag temperatures of the induction furnace. A possible explanation is that FeS, distributed between slag and metal, so as to produce equilibrium, takes part in one of these three reactions, new amounts diffuse from the metal into the slag and so forth. The reaction requires a high temperature and even then takes much time. This must be considered in connection with the possi-

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[1] Stahl und Eisen 29 (1909) Nr. 5.

bility of reversing all the above reactions by introducing small amounts of iron or manganese oxides:

(4) $CaS+FeO \rightleftarrows FeS+CaO$. This equation occurs from left to right for comparatively small amounts of oxygen, while from right to left it is the underlying principle of the three reactions, 1 to 3.

In all the foregoing reactions, one feature deserves the most important consideration, that is the high basicity of the slag; this, in turn, is made possible by the high temperatures attainable, especially in the arc furnaces. The law of mass action which is directly applicable to homogeneous reactions only, describes the effect of the high concentration of CaO. Whatever silicates and aluminates of iron and manganese, of nickel, chromium, and other alloys have been formed, they will be decomposed by its stronger base. This condition is also aimed at in the basic open-hearth. But it can not be carried to the same extent as in the electric furnace, because over 55% of CaO would result in a pretty dry viscous slag and because the oxides thrown out of solution would not find a sufficient quantity of a proper reducing agent. When as low as 12% to 13% of FeO and of MnO have been reached, it is considered the lowest metal content of an ordinary basic open-hearth slag, for low-carbon metal. Occasionally and besides in the pig and ore processes lower figures may be observed.

The elements, which in the present electric furnace practice, take care of reducing these oxides, are chiefly carbon in the arc furnace and silicon in the induction furnace. As already stated, the manganese is practically eliminated altogether, the FeO easily removed down to 0.5% FeO, nickel is reduced with great ease, chromium tungsten and vanadium according to their inherent amount of free energy with a larger consumption of power. Some of these elements are almost as liable to be oxidized by small quantities of oxygen as they are liable to be dissipated by volatilization, and in practical work some experience is required.

For explaining the mechanism of the reactions we avail ourselves of the advantage which was referred to in the introductory remarks, and which follows from our consideration of a system of various phases, so that we do not need to make any assumptions as to what definite chemical compounds we have to deal with. It is usual, for instance, to consider open-hearth slags as solutions of the other constituents, such as CaO, $Ca_4P_2O_9$, Al_2O_3, FeS, CaS a. s. o. in iron and manganese silicates as solvents. In our case we are gradually decomposing the solvent and are reducing its concentration to zero. It would not be of any advantage to know how the different constituents are combined with each other, even if it were possible at all, to answer such a question for molten solutions.[1]

It is of great importance, however, for the advancement of general metallurgical knowledge, to determine the melting point of the pure compounds and give the complete diagram of the melting point of their mutual solutions over as wide a range of concentrations as possible. Such work has been started in a splendid way by Vogt, Doelter, and others, but we need a great deal more data to make them suitable for practical use.

The melting points of

$FeSO_3$	are	1050°
$MnSiO_3$		1150°
$CaSiO_3$		1220°–1225°
Mg_2SiO_4		1400°

Most of the open-hearth slags seem to keep in the neighborhood of the eutectic composition, i. e. the one with the lowest melting point in those cases, where the compounds will form a eutectic. If one of the constituents is raised extraordinarily to a high concentration, the melting point as a rule goes up. Examples of this phenomenon are widely known, as, for instance, in the glass industry, the pure sodium and the pure potassium glasses as compared with the Na-K-glasses with a melting point lower than each of the other two, mixtures of sodium and potassium carbonate, etc. Acid slags become viscous, when the silica is artificially increased, basic slags increase their melting point with rising amounts of CaO, which can be easily raised over 75% under the influence of the arc without any fluorspar in the slag. As this mineral, which is used to a larger extent in American than in European practice is a good solvent, it prevents the use of an excessive temperature. It further permits to keep the concentration in SiO_2 low. While 12% to 20% SiO_2 are often contained in the high calcium slags, they can also be built up almost entirely from calcium iron and manganese compounds with very low SiO_2. One such slag, for instance, analyzed in its main constituents 39.10% CaO, 18.20% FeO, 13.80% MnO, and only 2.10% SiO_2. Such slags may be gaining in importance for special work.

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[1] Papers of James Hendrick (Journal Soc. Chem. Ind. 28, 775–778 (1909), *ibid.* 31, 520 f. (1911) and others, though very valuable for agricultural research, prove that chemical analysis alone can not solve the problems of the constitution of slags. Optical and thermal methods will have to be applied extensively.

The carbon thrown into the furnace and the carbon derived from the electrodes can produce several compounds. Prevalent among these are silicon carbide, calcium silicide and calcium carbide. This latter one seems to be the most persistent under operating conditions and is recognized by the development of acetylene from a cooled off sample. It is only after this carbide has been formed to a certain extent that the deoxidation of the charge can be relied upon as completed.

When this condition of the bath has been realized, the electric furnace represents the nearest approach to the ideal heterogeneous equilibrium between the different phases which has hitherto been accomplished in large scale metallurgy: converter and open-hearth are under the action of air and gas, the crucible metal takes carbon and silicon up, whilst in the electric furnace the action of the metal on the basic lining is almost nil, there is no exchange of elements between metal and slag. However, a small evaporation of participants of the slag takes place, and in this respect the induction furnace with its cold slag has a slight advantage over the arc furnace. Under certain working conditions of operations of an arc furnace, when it is thought advisable not to cover the electrode holes in the arch, airtight, fumes can be seen passing through the small joint between electrode and roof brick. These fumes always leave a deposit on the cooler parts of the electrodes, in powder form. An analysis of them taken during the oxidizing period of a furnace showed, aside from minor quantities of other substances, SiO_2 4.50%, FeO 8.49%, Fe_2O_3 60.60%, CaO 8.10%. This composition allows the conclusion that after reducing the metallic oxides from the slag there will be a considerable volatilization of CaO andsome less volatilization of SiO_2, both being probably first volatilized as elements and then oxidized in contact with the atmosphere. Smaller lots of Si may perhaps take part in the desulphurization by forming SiS_2, a volatile compound, and then decompose in contact with humid air or water.

In the foregoing we have discussed the points in which the chemical action of the slag of the electric furnace differs from the corresponding slags of other furnaces. What is to be said of the physical effect holds good in general, but it is important enough to be considered in connection with our former discussion. We have already seen, that there is by no means an ideal 2-dimensional surface between slag and metal and that both phases penetrate each other to a considerable extent. This is due to the various operations which the charge has to undergo from the time of its melting. The boiling in the oxidizing period intermingles small particles and reverses their mutual position. Upsetting of the whole charge often takes place when pouring from one furnace into a transfer ladle, and from there into another furnace. Then there are the effects of stirring, making additions, which have to drop through the slag into the metal, etc. One might think that a difference of specific gravities from 3 to 7.8 should produce a clear cut separation of the two phases by gravity, but the fact is that the separation proceeds astonishingly slow, even at higher temperatures, and with the more liquid state of the materials of the electric furnace. The prevailing picture that slag and metal behave like oil and water is only relatively true. The slag swims on the metal, but where small parts of the one are caught in larger masses of the other, they have to overcome an enormous friction. And the smaller a particle of slag is, the larger is its friction surface in proportion to its gravity, and the more time and effort will be required to overcome its adhesion to the glue-like iron walls which surround it from all sides. Following this up, there is every reason to believe that in dividing the particles of slag finer and finer, a point will be reached where the rising and separation of the slag particles would take such a length of time that all commercial advantage would be lost. If a stirring could be performed so as to agglomerate small particles into larger balls which would have a stronger tendency to rise, an important advantage would be gained. As long as we are not able to do this, we have to do the best we can by keeping the finished charge quiet and at a sufficiently high temperature to allow it to settle. Hereafter proper precautions have to be taken while teaming and pouring that the painstaking results of refining might not be reversed. But these matters are outside of the scope of the present paper.

This slow physical action may furnish a new explanation for the slow progress of the desulphurization as per equation No. 2 (page 8): The microscrope shows that silicious and sulphidic products are sometimes contained down to two-thirds, and even lower, from the top of an ingot. These non-metallic products appear as balls in the ingot structure and are elongated into a cigar-like shape after rolling or forging the metal. Although their melting point is lower than that of steel, they have not succeeded in uniting with the bulk of the slag in proper time. Consequently there is a lack of material in the slag, and desulphurizing can only take place whenever new sulphides are supplied. As the slag of the electric furnace allows to hold the metal, the sulphur can be removed to any desired extent.

A few words, however, may be said on the conditions obtained when the electric furnace is lined with more or less silicious materials. Probably as a result of the experiments of the late Thallner, the acid electric furnace has quite recently won some notoriety. An acid lining requires an acid slag, to keep the hearth in good condition. This acid slag will be much the same as the slag of an acid open-hearth as long as the charge is treated with an excess of oxides and the heat not exaggerated; if necessary it can be made to contain a higher percentage of SiO_2 for the same reasons which we set forth for highly basic slags. The great difference from the basic electric furnace is, in this case, that all four phases are in lively reaction with each other, that conditions approaching a status of equilibrium can not be reached and that the metal must be "caught" at a certain moment for teaming.

The solid and the metal phase react in this way, that carbon of the bath reduces Si from the hearth, the amount of Si present being regulated by a reaction between the two liquid phases, namely by keeping a sufficient stock of oxides in the slag to hold the Si within the required limits. The slag will therefore be a thoroughly black one, particularly during the beginning of the run. Thallner ascribes a specific beneficent effect to this exchange of Si and to the low heat conductivity of the silica lining. Towards the finishing of the acid heat the color of the slag clears up, and its reduction finally reaches a point where the glassy masses become light gray and green colored. Sulphur will, as in the acid open-hearth, remain unaltered in quantity, while phosphorus may be slightly decreased by phosphoric acid being thrown out of solution by the stronger SiO_2 and then reduced to phosphide of iron. This has to be confirmed, however, and it has to be explained, how this reaction can take place. Nothing definite can be said about it at the present time.

It may be that some of the advantages of this method are due to the mechanical property of the slag to agglomerate more easily than the basic slag particles to larger globules which force their way up to combine with the bulk of the slag.

While dealing with a subject of such highly actual interest as this one, I need hardly say that a complete discussion of every detail is impossible and would conflict with the commercial obligations of the author.

There are, however, so many points still open to discussion and open to scientific research that the author would feel glad if this paper should act as a stimulus to further research.

STUDY OF A SMALL CARBORUNDUM FURNACE

By Wilder D. Bancroft, L. V. Walker and C. F. Miller
Cornell University, Ithaca, N. Y.

In the runs to be described we have determined the amount of crystallized carborundum formed; but not the size of the crystals. While this last is important from the technical point of view it lay outside the scope of this paper, which is in itself merely a preliminary one. We have studied the yields in a 30 KW and a 20 KW experimental furnace, as affected by length of run. A granular carbon core was used for this series of experiments; but it is hoped some day to make runs with a graphite core, working with a lower voltage and a higher current.

At first the furnaces were built of Queen's Run fire brick, laid loosely together; but it was soon found more convenient to lay the bricks in mortar so as to prevent any possibility of the side walls breaking down during a long run. The furnace was 27″ in length, 16″ in width, and about 23″ in depth. The walls were 4″ thick, the width of a brick. The lower two bricks in the side walls were staggered so as to cut down the dead space.

The runs to be described were made with graphite electrodes 2″ x 4″ x 24″ clamped tightly in water-cooled electrode holders designed by Mr. Gillett and made by Champaign Brothers of Ithaca. They consist of a plate 8″ x 4″ x 7-8″ to which is attached a box four inches square and two inches deep. Through the cover of this box there pass two tubes each of 1-4″ bore. One tube passes just through the cover and the other nearly to the bottom of the box, water being let in through the second pipe and out through the first. The electrode holders are made of cast bronze and when two are clamped on opposite sides of an electrode, there is a possibility of 32 sq. in. of cooling surface. By putting a thermometer at the inlet tube and another at the outlet tube it is easy to determine radiation losses provided one weighs the water which has passed through the electrode holders. With a moderate volume of water flowing, the electrodes can be kept fairly cool even with a current of 1000 amperes or more.

In the first run, we made the mistake of bolting the electrode holders to the electrodes some little distance from the furnace walls with the result that a marked disintegration of the electrodes took place. In the next run the electrode holders were shoved close against the furnace walls.

The electrodes passed through the end walls of the furnace at a point central to the cross-section of the charged furnace, and extended a distance of 5.5 inches within the furnace walls making direct contact with a 4 lb. granular carbon core, two inches wide, four inches deep, and 16 inches long.

The materials used in the charge were as follows:

Sand: White sand supplied by the Carborundum Co.

Analysis: 99.4% SiO_2; 0.4% residue H. F. treatment; 0.2% loss on ignition.

Coke: Supplied ground to 14 mesh by the Acheson Graphite Co.

Analysis: 10% ash; 3% moisture; 83% total carbon; 4% volatile.

Sawdust:

Analysis: 38% carbon.

Commercial salt.

The normal change was: sand 53.5%; coke, 40%; sawdust, 5%; and salt, 1.5%; 190–200 lbs. being used in each run. This composition corresponds to a 10% excess of carbon over that as calculated from the equation,

$$SiO_2+3C=SiC+2CO.$$

It has been found by experiment that the 10% excess of carbon is required to prevent the formation of silicon carbide within the core. If the coke used in the charge were all available and were neither so fine as to be removed by escaping CO nor so large as to become silicon-coated instead of being converted into carborundum, this excess would not be necessary.

The power available in the electrochemical laboratory consists of a G. E. motor generator, form K, type 1, 60-cycle, 2200-volt 150-h. p. induction motor with starting compensator; the motor is directly coupled to a form A, class 6, 2000–ampere, 35-volt, 27.4-cycle, 75-h. p., double-current generator, from which alternating current is drawn through a form B-1, type OO, 150-h. p. oil transformer. The generator is separately excited by a form

H, class 2, 125-volt, 26-ampere D. C. generator. With such an apparatus, by suitable adjustment of a the transformer ratios, any voltage from 25 to 200 was obtainable in steps of about 1 volt. The voltage across the furnace was read on a Thomson double-scale voltmeter, and the current on a 2100-ampere Leeds and Northrup mercury ammeter. Owing to an accident to the ammeter a few of the runs were made using a current transformer having a ratio of 1:45.5 connected in series with the furnace and the current calculated from observations on a 30-ampere Thomson instrument.

In every experiment the normal charge was weighed out to total 200 lbs. and intimately mixed. It was then placed in the furnace even with the bottom of the electrodes. Two pieces of sheet-iron were then placed on each side of the electrodes, thus forming a rectangular cavity in which to place the crushed carbon core. The sheet-iron can be held in place by packing some of the charge against the outer sides. It is very important to pack that part of the charge in which the core rests, as even at best there is sure to be a considerable settling of the core as the run proceeds, which will alter the core shape. It is interesting to note here that were other shapes of core desirable a very convenient method for working would be to use paper forms, as the paper will soon burn off and introduces no new variables. The rest of the charge was then added; sheet-iron plates carefully removed so as not to alter the core shape, and then the charge built up so as to conform to the outer surface of a watermelon, it being observed after the first run that the heat radiation follows such a curve.

In practically all the efficiency runs, in order to check the conditions as closely as possible, temperatures were read at the core, using all three high-temperature instruments at hand, the Thwing, Wanner, and Morse, which are fully described in Dr. Gillett's paper on high-temperature measurements.[1] This was made possible by the use of Gillett's temperature tube for use in carborundum furnaces, which is also fully described in the above article. It was found that a brass tube, inserted in the end of the carbon tube and attached at the other end to a flexible

[1] **Jour. Phys. Chem. *15*, 213 (1911).**

metal tube, gave better satisfaction than the glass-rubber connection used by Gillett, there being less chance of fracture in handling the suction tubes from which silica deposits must be removed at intervals in order to keep the tubes from clogging. When building the furnace a Gillett tube was placed so that the graphite plug rested directly against the core, midway between the two electrodes, the tube being supported by the charge and also, at the suction end, by a hole drilled in the brick wall through which the tube extended for about half an inch. The composition of the tube changes with the run, being partially converted into carborundum. In order to keep the results strictly comparable, a new tube was made for each run.

As an interesting check on the rate of heating a Pt-PtRh thermocouple was placed 8 inches to the left of the Gillett temperature tube and 4.5 inches from the core. Readings were taken every 5-10 minutes throughout the run. The data are given in Table I.

TABLE I

30 KW run, 8 hours

Time	Amp.	Volts	Core Temp. °C.	Thermocouple °C.	KW obs.
10.00	10	160			1.6
.05	50	160			8.0
.10	25	160	1250	20	3.5
.15	200	160	1360		32.0
.20	310	92			28.5
.25	325	72	1760		23.4
.30	400	78	2240		31.2
.35	475	72	2250	20	34.2
.40	500	64		40	32.0
.45	510	59	2400	50	30.1
.50	530	56	2400	60	29.7
.55	550	54		60	29.7
11.00	560	53	2420	60	29.7
.05	570	52		70	29.7
.10	590	50	2460	75	29.5
.15	600	50		90	30.0
.20	605	49	2490	100	29.6

TABLE I—*Continued*
30 KW run, 8 hours

Time	Amp.	Volts	Core Temp. °C.	Thermo-couple °C.	KW obs.
.30	635	47		150	29.8
.35	660	47	2490	185	31.0
.40	640	45		225	28.8
.45	630	45		260	28.4
.50	640	44	2520	315	28.2
.55	670	45		330	30.1
12.00	680	44	2550	385	29.9
.05	680	44		430	29.9
.10	695	43		475	29.9
.15	690	42	2550	550	29.0
.20	690	42		590	29.0
.25	705	43		620	30.3
.30	735	43			31.6
.40	710	41	2550	745	29.1
.45	735	42		790	30.9
.50	740	42			31.1
.55	720	40		880	28.8
1.00	725	41	2550	895	29.7
.05	720	41			29.5
.10	740	41		965	30.3
.15	740	40	2520	1010	29.6
.20	740	40		1035	29.6
.25	735	40		1065	29.4
.30	750	40		1090	30.0
.35	760	40	2500	1130	30.4
.40	770	40		1150	30.8
.45	765	40			30.6
.50	765	40		1195	30.6
.55	775	40	2460	1225	31.0
2.00	770	40	(fumes)	1250	30.8
.05	775	40		1270	31.0
.10	760	39	2350	1300	29.6
.15	770	39	(fumes)		30.0
.20	760	39		1335	29.6
.25	770	39		1360	30.0
.30	770	39		1380	30.0
.35	765	39	2500	1390	29.8
.40	760	39		1400	29.6
.45	760	39		Limit of	29.6

TABLE I—*Continued*

30 KW run, 8 hours

Time	Amp.	Volts	Core Temp. °C.	Thermo-couple °C.	KW obs.
.50	755	39	2500	PtRh thermo-couple	29.4
.55	760	39			29.6
3.00	760	39			29.6
.05	775	40	2480		31.0
.10	780	40	Small carbon tube burned out		31.2
.15	760	39			29.6
.20	760	39			29.6
.25	760	39			29.6
.30	760	40			30.4
.35	760	40			30.4
.40	760	40			30.4
.50	775	40			31.0
.55	755	40			30.2
4.00	760	40			30.4
.05	750	40			30.0
.10	740	39			28.9
.15	740	40			29.6
.20	750	40			30.0
.25	760	40			30.4
.30	760	40			30.4
.35	760	40			30.4
.40	760	40			30.4
.45	765	40			30.6
.50	760	40			30.4
.55	755	40			30.2
5.00	755	40			30.2
.05	760	40			30.6
.10	750	40			30
.15	780	41			32
.20	750	40			30.0
.25	750	40			30.0
.30	740	40			29.6
.35	735	40			29.4
.40	735	40			29.4
.45	735	40			29.4
.50	720	40			28.8
.55	750	40			30.0
6.00	740	40			29.6

Summary

Core	3.75 lbs.
Charge	198 “

Yield

Siloxicon	72.0 lbs.
Unchanged Charge	61.0 “
Graphite	3.5 “
SiC	12.75 “

Owing to the fact that accurate wattmeters are not made, which are adjustable to widely varying currents and voltages, and since it seemed inadvisable to purchase apparatus that could perhaps be used for only the one research, no corrections have been made for power factor, and all that we have calculated as input is ‘observed’ kilowatt hours. The average ‘observed’ kilowatts were taken for a given interval and were calculated to kilowatt hours. The sum of all these observations gives the total kilowatt hours input for the run. Dividing the grams of carborundum formed by the input gives mean grams of carborundum formed per kilowatt hour. The data are given in Table II.

TABLE II

30 KW run, 8 hours.

		Calc. of KWH Input.			
Average KW observed	KWH	Average KW observed	KWH	Average KW observed	KWH
4.8	0.40	30.6	2.55	31.0	2.58
5.8	0.48	30.7	2.56	31.0	2.58
15.8	1.32	30.6	2.55	30.0	2.50
30.2	2.52	30.8	2.57	29.8	2.48
26.0	2.16	30.9	2.57	29.5	2.46
27.3	2.28	30.9	2.57	29.4	2.45
32.7	2.72	29.8	2.48	29.4	2.45
33.1	2.76	29.8	2.48	29.1	2.42
31.1	2.59	29.8	2.48	29.4	2.45
29.9	2.49	29.8	2.48	29.8	2.48
29.7	2.47	30.0	2.50		
29.7	2.47	29.9	2.49	Total	234.36

TABLE II—*Continued*

3– KW run, 8 hours

Average KW observed	KWH	Calc. of KWH Input.			
		Average KW observed	KWH	Average KW observed	KWH
29.7	2.47	29.7	2.47		
29.6	2.46	29.6	2.46	KWH. input Carborundum 24.7 g KWH	
29.8	2.48	29.5	2.46		
29.8	2.48	29.5	2.46		
29.7	2.47	29.6	2.48		
29.7	2.47	29.8	2.48		
30.4	2.53	31.1	2.59		
29.9	2.49	29.9	2.49		
28.6	2.38	29.6	2.46		
28.3	2.36	29.6	2.46		
29.1	2.42	30.0	2.50		
30.0	2.50	30.4	2.53		
29.9	2.49	30.4	2.53		
29.9	2.49	30.4	2.53		
29.5	2.46	30.7	2.56		
29.0	2.42	30.6	2.55		
29.6	2.46	30.3	2.52		
31.0	2.58	30.2	2.52		
31.0	2.58	29.5	2.46		
29.8	2.48	30.0	2.50		
30.0	2.50	29.8	2.48		
31.0	2.58	30.2	2.52		
29.9	2.49	30.4	2.53		
29.2	2.43	30.4	2.53		
29.6	2.46	30.4	2.53		
29.9	2.49	30.5	2.54		
29.9	2.49	30.5	2.54		
29.6	2.46	30.3	2.52		
29.5	2.46	30.2	2.52		
29.7	2.47	30.4	2.53		
30.2	2.52	30.3	2.52		

One of the pleasant things about this research was that absolutely no difficulty was experienced in separating the products of the run. Consequently it is reasonable to claim a fair amount of accuracy in recording yields. The furnace is usually cool enough to dismantle 36-48 hours after the run is over. The first coat to be removed is a thin crust of fused sand covering the charge, which is always rigid enough to be skimmed off readily with the hand. The unchanged charge is next in order and, being powdery, has to be removed with a scoop. By forcing a scoop-shaped pan under the siloxicon layer, which presents a greenish-gray appearance, and then extracting the electrodes carefully, siloxicon, carborundum, graphite, and core can be removed together and will remain intact. Some of the core, however, becomes graphitized, so that the core settles a great deal, leaving an open space between the upper formation of crystallized graphite and the core. When the stationary stage has been reached in the furnace, a cross-section through the center of the furnace perpendicular to the core shows concentric cylinders of graphite, carborundum and siloxicon whose wall thicknesses are 2″, and 3″ respectively. This wall thickness falls off gradually towards the end walls of the furnace, which indicates very clearly the heat gradient throughout the furnace. The carborundum layer is the most rigid, so that the siloxicon can be easily separated from it by hand, the line of demarcation being the point where the sharp SiC crystals prick the hand. The graphite is removed from the other side of the carborundum layer by brushing with a test-tube brush, and whatever graphite remains with the core can be sifted out through a 14-mesh sieve. This method of separation proved sufficiently accurate, in that runs could be duplicated almost exactly, the yields never varying more than an ounce or two. A summary of the results is given in Table III.

TABLE III

Summary of efficiency runs

30 KW series

No.	Time of run (hours)	Charge (pounds)	Core (pounds)	Graphite (pounds)	Siloxicon (pounds)	SiC (pounds)	Grams SiC per KWH
1	2.0	180	4	0.75	16.75	5.00	40.2
2	2.5	190	4	0.75	17.00	7.50	47.5
3	3.0	195	4	1.00	24.50	8.00	47.1
4	3.5	190	4	1.37	27.00	9.00	44.5
5	4.0	193	4	1.50	30.00	10.00	42.5
6	4.5	197	4	2.37	34.50	11.00	39.2
7	6.0	198	4	3.25	51.00	12.75	31.8
8	8.0	198	4	3.50	72.00	12.75	24.7
20 KW series.							
1	2.5	200	4	0.62	13.00	2.75	25.3
2	3.5	200	4	0.87	19.00	3.87	25.4
3	6.0	200	4	1.87	26.50	7.87	29.0
4	10.0	200	4	3.25	47.00	12.75	23.5
5	14.0	199	4	3.75	72.00	10.25	16.3

From the data for the two series of runs, together with that for the 30KW, 8-hour run taken as a typical experiment, curves have been plotted to show the furnace regulation, variation in temperatures at the core and at the surface of the furnace with the time, the rate of increase in the total yield, and the yield in grams per KWH for different periods of run.

In a typical run the potential drop across the furnace is raised rapidly to about 160 volts and is held there until the furnace is brought up to load and is then lowered as much as is necessary to keep the heating rate constant at the desired value. In about half an hour the voltage can usually be dropped to 50 volts and from then on there is a gradual drop in potential corresponding to a similarly gradual increase in the current. Hence in a very short time from the start the furnace regulation becomes a simple matter. This is in agreement with the curve, Fig. 1, showing the core temperatures at different intervals throughout the run. The rise in core temperature is very rapid during the first 30-60 minutes, and from then on the temperature remains nearly constant. To show that the rate of heating in different runs approximates similar conditions, there are given in Fig 2

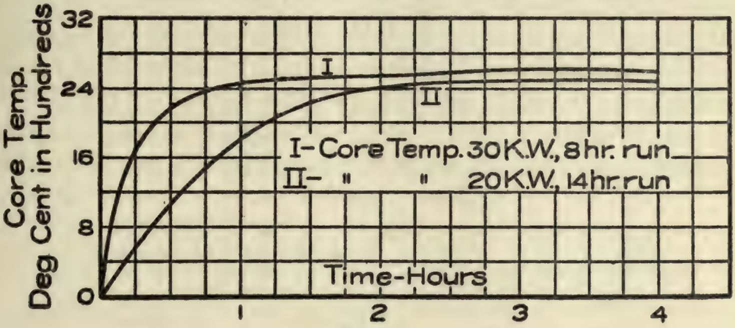


Fig. 1

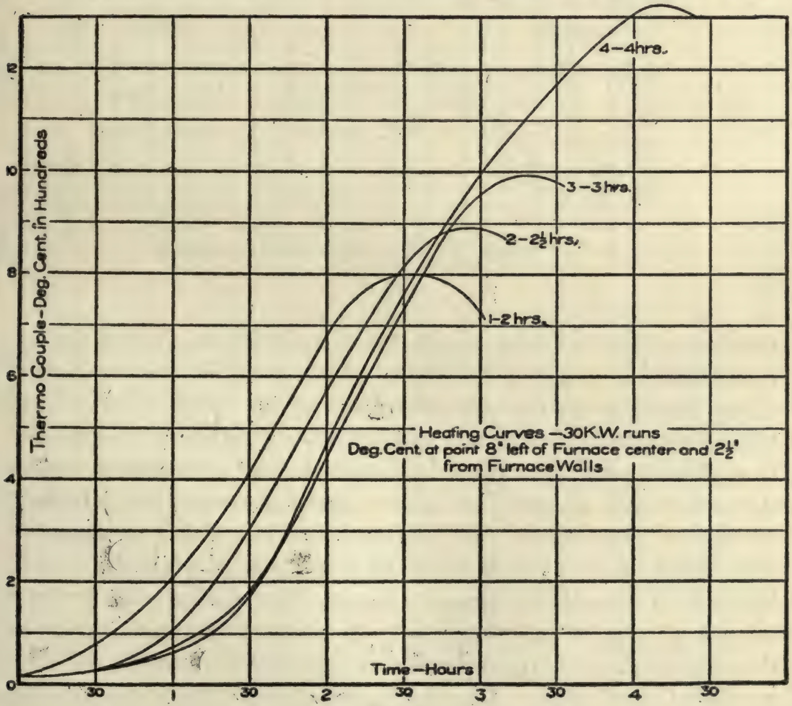


Fig. 2

curves showing the rise in temperature at a point 8″ to the left of the core center and 4.5″ from the core. A very gradual even rise in temperature is characteristic of these curves.

We now come to a consideration of yields. In Fig 3. are the yields in pounds of carborundum, siloxicon, and graphite for the 30 KW furnace, while the corresponding results for the 20 KW furnace are given in Fig. 4. The formation of graphite appears to follow approximately a straight line curve for some time, and then starts to bend at about the time that the carborundum formation has reached its limit. The siloxicon curves show a slight bend in the opposite direction at this same point. It is almost self-evident that this would be the case, owing to the fact that the carborundum layer has arrived at a maximum radiation surface as well as at a maximum temperature and hence is most efficient in heating the siloxicon and unchanged charge about it. The slight decrease in the rate of formation of graphite is hard to explain except by the stationary-stage theory, as there is always a layer of carborundum which could furnish carbon on decomposing, also an excess of carbon in the core itself. It may be that the carbon in the core is not as available owing to the

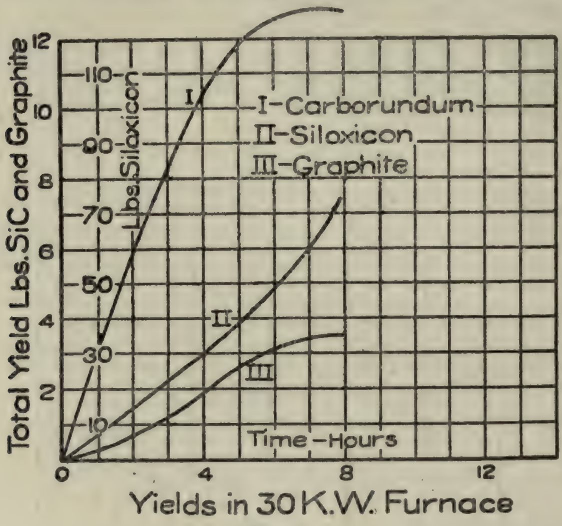
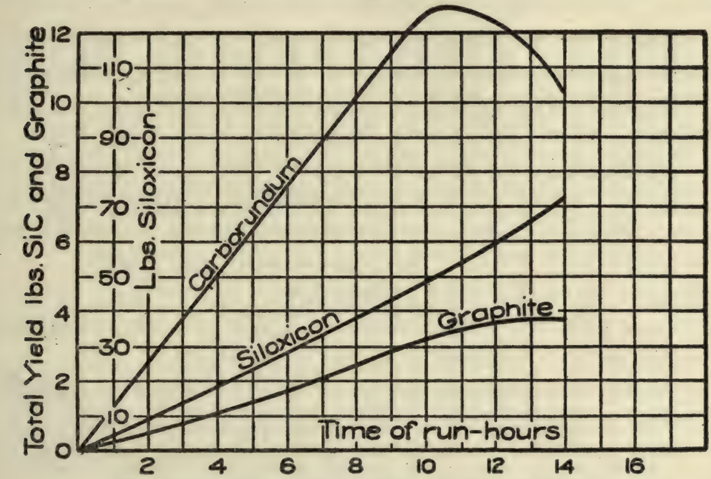


Fig. 3

size of the granules. This bend might also be explained as experimental error were there not a striking resemblance in the graphite curve both of the 20 KW and of the 30 KW furnace.

As was anticipated from the beginning, the carborundum curves show a flat, indicating that at this point the heat given off by the SiC is equal to the calories received from the graphite and core, none of the energy being expended to raise the temperature of the SiC layer. This is the beginning of the stationary stage.



Curves showing yields in 20 KW Furnace

Fig. 4

In the 30 KW. furnace we reach such a point in 6 hours of run, Fig. 5; in the 20 KW furnace at the end of 10 hours. The 14-hour run on the 20 KW furnace shows that the conditions for a stationary stage are by no means permanent in the carborundum furnace, and that there is such a thing as a rapid decomposition of SiC if the run be continued too long. This could be explained as due to the high heat-insulating effect of the then rapidly increasing siloxicon yield which would confine more heat in the SiC zone, causing the SiC to decompose at an increased rate. It is unfortunate that a 12-hour, 20 KW run could not have been made, or else a longer run on the 30 KW furnace, in order to verify our results on this point.

The curves showing the relative SiC yields for the two rates of heating, Fig. 6, make it at once evident that, the quality yield being equal, a 6-hour run at 30 KW is cheaper than a 10-hour run at 20 KW. On the other hand at the end of 6-$\frac{3}{4}$ hours the 20 KW furnace is giving the same efficiency as the 30 KW one, and shows a higher efficiency from that point on. This would indicate that for long periods of run the 20 KW furnace would have the advantage, provided the efficiency of the 30 KW furnace continues to fall off at the same rate.

With the furnace of the dimensions we used, 30 KW is really rather too much as the bricks began to soften towards the end of the run. It is a very good size for a 20 KW run and would probably work well at 25 KW; but we have no data on this point.

In connection with these runs we have collected data in regard to heat losses with graphite electrodes and with carbon electrodes; but these will form the subject of another paper at some future time.

The general results of this paper are:

1. A furnace has been devised in which it is possible to duplicate results with a satisfactory degree of accuracy.
2. We have made a study of yields in a 20 KW and a 30 KW furnace of specified dimensions, using a carbon core.
3. Curves are given for core temperatures during a run, and for temperatures in one other part of the furnace.
4. Curves are given for absolute yields of graphite, carborundum, and siloxicon for different lengths of run.
5. Curves are given for yield of carborundum per kilowatt hour under different lengths of run.

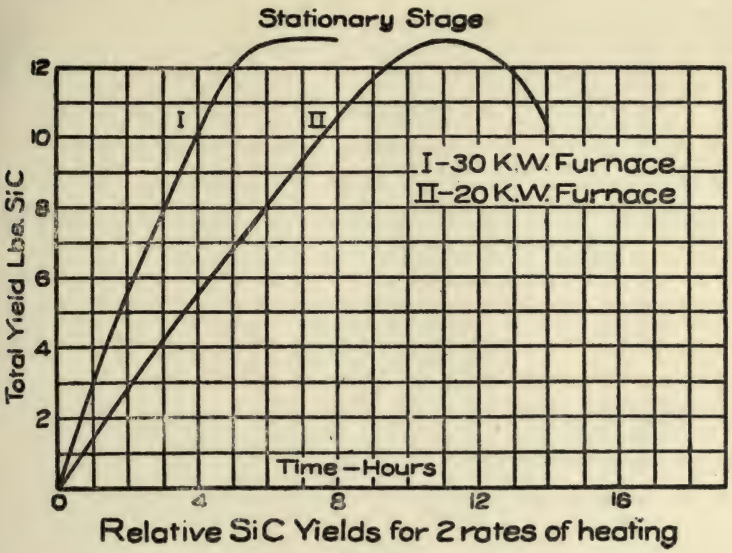

Stationary Stage
12
10
8
6
4
2
Total Yield Lbs. SiC
I
II
I–30 K.W. Furnace
II–20 K.W. Furnace
Time—Hours
0
4
8
12
16
Relative SiC Yields for 2 rates of heating

Fig. 5

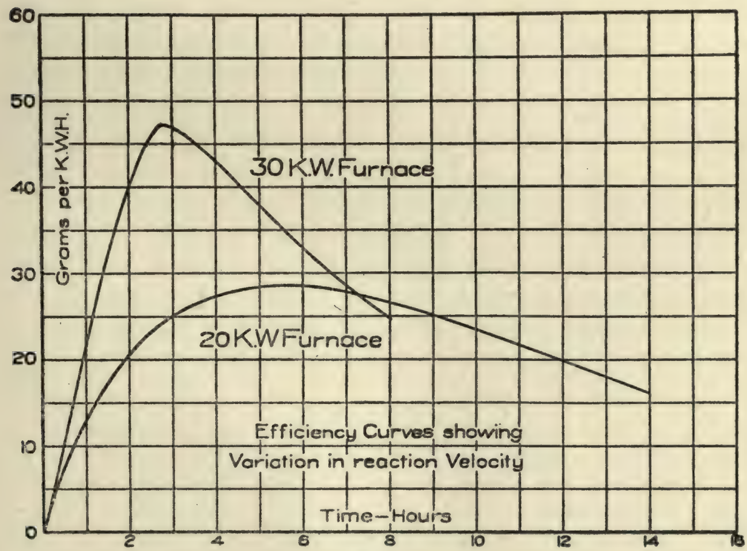

60
50
40
30
20
10
0
Grams per K.W.H.
30 K.W. Furnace
20 K.W Furnace
Efficiency Curves showing
Variation in reaction Velocity
Time—Hours
2
4
6
8
10
12
14
16

Fig. 6

(*Abstract*)

A REFRACTORY MATERIAL FOR HIGH TEMPERATURE AND LABORATORY WORK

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The demand for a refractory material to withstand excessive temperatures obtained in laboratory and experimental work has required the development of a material having higher refractory properties than those heretofore available. Fused alumina made in the electric arc furnace by fusing bauxite, a natural hydrate of alumina, has been used as an abrasive material under the trade name of "Alundum" for some time. This material has also been found to possess very desirable refractory properties when made up into various forms. This is done by crushing the alumina, grading to a uniform mesh and mixing with a small amount of a highly refractory ceramic bonding material, shaping by casting or moulding and burning at a high temperature in a porcelain kiln.

The properties which make fused alumina desirable have been outlined by Mr. L. E. Saunders in the Transactions of the Electrochemical Society, Vol. 19, page 333 (1911), as follows:—

It is between 9 and 10 in the scale of hardness, has a melting point of 2050°C., a thermal conductivity of 2.1 times that of fire-clay, an electrical conductivity at various temperatures as follows:—

At	520	degrees	C.	the resistance is	130.	megohms
"	730	"	C.	"	16.	"
"	892	"	C.	"	5.3	"
"	1020	"	C.	"	1.8	"

Specific heat between 20° and 100° C. is .198. Being neither strongly acid nor basic it is not chemically active even at elevated temperatures. The thermal conductivity has been found to be a linear function .0000078 per degree centigrade. It can be made with a maximum tensile strength of 1700 per square inch and the porosity of the various mixtures can be changed to suit the requirements which allows it to be used for filtration purposes. Its practical use has been for linings of the electric furnaces of the wire resistance type, muffles, tubes, cores and other shapes. Refractory crucibles for melting platinum and for standardizing thermocouples, combustion boats for the determination of carbon in steel and similar work have been used repeatedly. Non-porous pyrometer tubes for high temperature work, refractory cement, porous extraction thimbles, filtering crucibles and cones for analytical work, filtering plates, dishes, etc., have been made of this material and have the advantage of being highly refractory, having a high thermal conductivity, being chemically inactive and being of easily controlled porosity and composition for any particular purpose.

HEAT LOSSES IN FURNACES

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In any kind of furnace the question of preventing the loss of heat is important, for no matter how the heat is obtained it costs something and consequently, other things equal, that furnace is most desirable which uses the greatest percentage of the total heat generated for the particular object in view. In the furnace which uses electricity for the generation of heat the importance of preventing losses of heat is very much greater than in any other. To generate 1000 kilogram Calories requires an expenditure of 1.16 kilowatt hours, and consequently the cost per calorie is always expensive when electricity is used for heating.

In heating any material in a furnace a general rule is that the generation of heat should be as rapid as possible. In any given furnace the heat losses may be expressed as so many watts, and, therefore, the longer it takes to heat the furnace charge the greater the losses will be. Suppose that a furnace contains a charge to be heated to 1500 degrees centigrade and that the average loss of heat is at the rate of 100 kilowatts, then if the process of heating the charge takes 1 hour the losses will amount to 100 kilowatt hours; but if by using a more rapid generation of energy the charge can be heated in 30 minutes the losses will amount to 50 kilowatt hours.

An example from experiments on a certain process may be given to illustrate this point. The problem was simply to heat a furnace charge to a certain temperature and experiments were made to determine the effect of increasing the rate of generation of energy and comparing the kilowatt hours required to heat a given charge. Here are typical results:—

Rate of generation of energy.	Energy per kilogram of product.
88 kilowatts	1.7 kw. hours.
93 kilowatts	1.6 kw. hours.

Thus by increasing the rate of generation of energy by 5.7 per cent. the energy consumption was reduced 5.9 per cent.

This particular example is only a laboratory scale experiment, but it serves to illustrate the point, that in the design of an electric furnace one of the first things to consider in avoiding heat losses is to make the rate of generation of energy per unit volume of charge as high as is compatible with other considerations, for in this way the saving of heat losses may be largely prevented. In the example given above the actual saving involved working commercially and expressed in money amounts to $1250 a year.

Another point of great importance in furnace design in order to avoid heat losses is to keep the external surface of the furnace as small as possible. This is so very obvious that it seems almost an impertinence to mention it, but anyone who will take the trouble to study commercial furnaces of various sorts will find that this very point by no means receives the attention it deserves. Moreover, there does not appear to be any published information on what may actually be done in this way, so that the results of an actual experiment will be of interest.

In a resistance furnace using 746 kilowatts the charge was heated to a temperature somewhat above 2000 degrees C., and maintained at that temperature for some hours. The furnace as originally constructed had an outside surface of 80 square meters, excluding the foundation. The design was afterwards changed so that the outside surface was 53 square meters. Determinations of the energy consumption per kilogram with the two designs of furnace give the following results:—

	Surface of Furnace	Energy per kg. of product
	80 square meters	6.1 kilowatt hours
	53 square meters	5.0 kilowatt hours
Reduction	34 per cent	18 per cent

Having done all that is possible in the way of perfecting the design of the furnace so as to avoid unnecessary heat losses the final step is to provide the best heat insulation possible. Heat losses occur in various ways, but experience seems to show that the most serious losses are through the furnace body. Here the heat escapes in three ways:—(1) Conduction, (2) Convention,

(3) Radiation. It is highly desirable that all these methods of loss should be studied, but at the present time the necessary data are lacking. A study of each source of heat loss is difficult and will involve much time.

In view of these considerations it was thought desirable to make experiments as to the relative heat losses which occur with various materials, some commonly used in furnace construction and some specially made for heat insulating purposes.

In order to do this furnaces were constructed which have been described in detail elsewhere(1). These consisted essentially of hollow cubes with sides of 230 mm. while the hollow spaces were cubes with sides of approximately 110 mm, so that the thickness of the walls of the hollow cubes were 60 mm. The furnaces were supported on knife edges so that all sides were exposed to the air. Through small holes in the furnaces wires entered to carry electric current to resistors of nichrome wire, and other holes in the furnace permitted the insertion of a thermocouple, by means of which the interior temperature could be determined.

In making an experiment a current was passed through the resistor and so regulated that the temperature was maintained constant. When equilibrium was reached the temperature and rate of generation of energy was noted, this giving the amount of heat escaping through the furnace walls at that temperature.

The results of several experiments are given in the following table:

TABLE

Temperatures	Degrees			Remarks
	500 Watts	700 Watts	800 Watts	
Fire brick 1	460	760	910	Good quality.
Fire brick 2	485	780	950	Good quality.
Fire brick 3	425	705	860	Cheap brick.
Fire brick 3 with insulating jacket 25 mm. thick	180	315	400	Special asbestos insulation.
Fire brick 4	430	685	810	
Fire brick 4 painted with lampblack	455	720	865	
Fire brick 4 painted with aluminum	370	600	725	
Silica brick	565	920	1100	Extrapolated at 800 deg.
Magnesia brick	860	...	....	At 400 deg. C. loss was 580 watts.
Red building brick	280	460	565	
Insulating building brick	245	380	460	
Kieselguhr brick	130	220	275	

In the first column are given the materials of which the furnace was constructed and in the second, third and fourth columns the heat losses at 500 deg. C., 700 deg. C. and 800 deg. C. respectively.

It is interesting to note in this table the effect of the nature of the outside surface of the furnace on the heat losses in the case of Fire brick 4. It also appears that silica and magnesia brick are far from satisfactory insulators, and if they must be used in furnace construction on account of their refractory qualities they should be backed up with a better heat insulator.

Red building brick and the special heat insulating building brick are fairly good insulators, but by no means as good as the kieselguhr brick. A comparatively thin jacket of specially prepared asbestos in the case of Fire brick 3 caused a very marked diminution in the heat losses.

As regards the saving in heat losses with large furnaces; one experiment may be quoted. The total outside surface of the furnace exposed to the air amounted to 20 square meters. The furnace was heated by means of a resistor and it was possible to make determinations of the heat losses at various temperatures. It was found that at 1100 degrees C. the loss amounted to 38 kilowatts. Observation showed that there was considerable differences in the temperatures of the outside walls. About 4 square meters of those parts of the outside of the furnace which were hottest were covered with the "Insulating building brick" referred to in the table above and another determination of the heat losses made, which showed that these now amounted to 32 kilowatts.

A METHOD FOR TESTING THE MUTUAL CORROSIVE EFFECT OF METALS

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It is being widely recognized that the acid test, as a measure of the resistance of iron and steel to corrosion under normal conditions, is unreliable and deceptive. Whipple & Whipple emphasize this in an article before this Congress. A trustworthy method of determining this resistance is highly desirable. A test for determining the relative values of paint films as protective coatings for iron and steel, devised by one of the authors, Walker and Lewis, Jour. Ind. Eng. Chem., *1*, 11. (1909), developed by the late Mr. M. T. Jones, and used by Mr. W. C. Slade, W. C. Slade, Ibid., 4, 189 (1912), is applicable to the study of the influence of one metal on the corrosion of another with which it is in contact, allowing the use of neutral solutions, if necessary of pure water, or of a particular water whose action it is desired to predict. The method consists in connecting electrodes of the two metals through an ammeter, keeping the solution about the electronegative metal saturated with air, and measuring the current in the external circuit.

The value of the electrolytic theory for correlating and utilizing the facts and phenomena of corrosion is underestimated by many, through lack of appreciation of the number and importance of the factors involved. At least three of these factors play controlling parts in all processes of atmospheric corrosion.

1.–The electrolytic potential determines the direction of the reaction, though seldom the rate of corrosion. Thus pure zinc is strongly electropositive, and yet its rate of solution, even in relatively strong acids is very low, owing to the polarization encountered.

2.–The ease of deposition of hydrogen upon the metal determines whether and how fast a metal electropositive to hydrogen will corrode in water in the absence of air, and probably plays a large part in atmospheric corrosion, although it has hitherto been impossible to separate this effect from the phenomena of depolarization.

3.–In the atmospheric corrosion of most electropositive metals the catalytic effect of the surface on the hydrogen oxygen reaction, i. e. upon the depolarization, seems to determine the rate of reaction.

The influence of one metal on the corrosion of another is the sum-total of these effects. The action is always accompanied by the flow of current, and is proportional thereto: it is suggested to measure that current, under conditions as similar as possible to those of practice. While it is not claimed that these figures have theoretical significance, they can, with proper attention to detail, be given distinct value for purposes of comparison. The size of the electrodes must be uniform, especially that of the electronegative metal, as the depolarization and hence the current is proportional to its area. The distance of the electrodes, the concentration of the electrolyte, the resistance of the external circuit, and the temperature must be kept constant. In a short time the surface of the electronegative metal becomes coated with hydroxide which has migrated thither from the other electrode, and which cuts down the current, due perhaps to the ohmic resistance introduced, perhaps to poisoning of the catalysis. The electrodes must be freshly cleaned before each reading. The air supply is important, as the electropositive metal rapidly exhausts the oxygen from the water about the other electrode, necessitating constant replenishing.

The above points are well illustrated in the case of zinc and iron. The electrodes used were rods $\frac{1}{2}$ inch in diameter with an exposed surface 1 inch long. They were immersed in a N-KCl solution, at a distance of 2 inches. The current, when above one milliampere, was measured by an ammeter of 30 milliampere scale deflection, and 10 ohms internal resistance, while below this limit an instrument of a total range of 1 milliampere, and of 100 ohms resistance was employed. We did not have at our disposal two instruments of suitable range, of equal resistance. That the influence of resistance was small, is shown by the fact that for currents below one milliampere the introduction of an additional one hundred ohms changed the current by less than one-tenth unit. These arbitrary standards were fixed after preliminary tests, for the sake of uniformity in these respects.

When fresh electrodes are immersed, there is a strong first swing of the galvanometer, the reading decreasing rapidly, and then more slowly. After from two to four minutes the rate of diminution, though never zero, becomes very small. The magnitude of the first swing is probably determined by the potential difference between the electrodes, the closing of the circuit offering a fresh area for the unrestricted deposition of hydrogen. The current is rapidly reduced by polarization, and soon reaches a fixed value representing equilibrium between hydrogen deposition and the diffusion to the electrode of the oxygen necessary for its depolarization. This current is the value we propose to use. In a short time there is in addition, as we have already stated, a deposition on the depolarizing surface of hydrate from the other electrode, the ohmic resistance is increased and the current continues to fall. All values in this article were taken at the end of the first rapid drop. Washing and wiping the depolarizing surface is sufficient to reproduce the phenomena and the readings. The experimental accuracy obtained is indicated by the deviation of the individual observations from the curves.

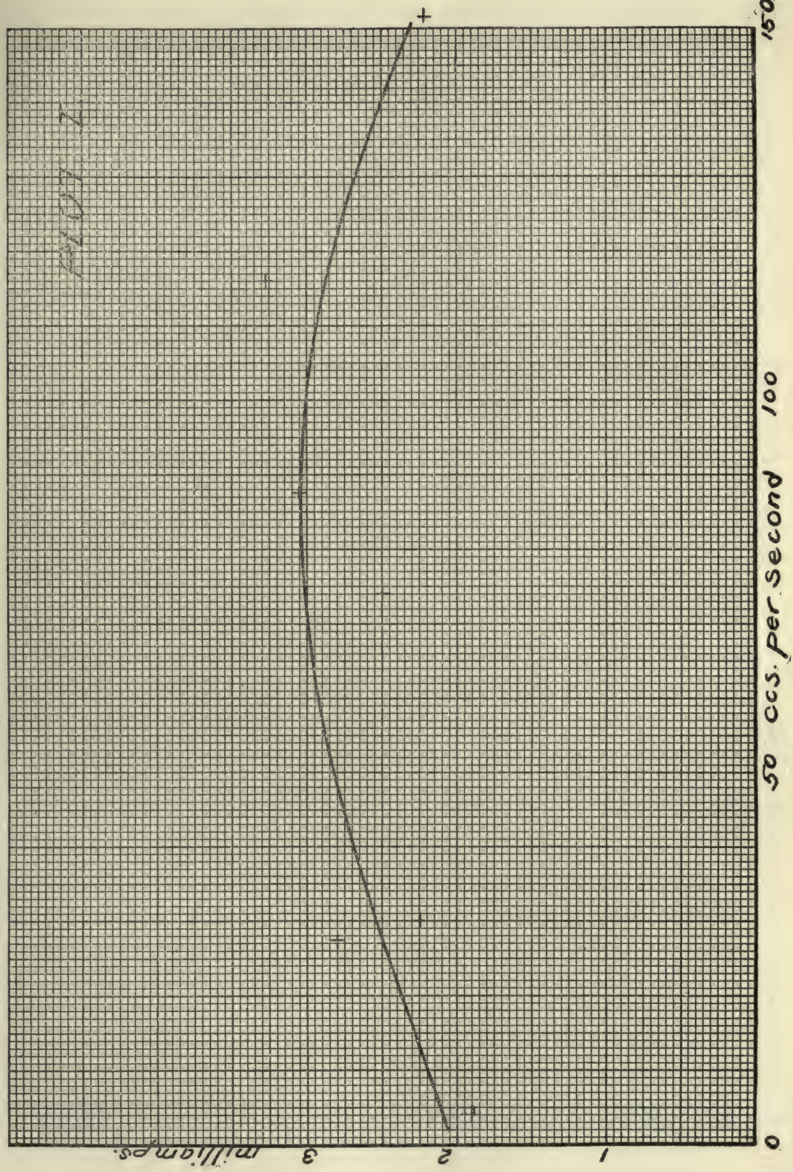
To show the influence of the air supply on the current obtained, measurements were made with zinc and iron electrodes, varying the amount of air bubbled about the iron. The results are shown in Plot I. The current rises distinctly with increase of air up to a definite maximum, beyond which it begins to fall. The decrease is probably due to the high resistance introduced into the circuit by the lack of continuity of the solution when excessive air is used. For our further work, the rate approximated one hundred cubic centimeters per second.

To illustrate the utility of the method, tests were made of the action of alloys of zinc and copper on the corrosion of iron. The results are shown in Plot II. The runs were further continued, and at the end of a week the values shown in Plot III were obtained. All alloys containing appreciable amounts of copper have decreased in protective capacity, those above twenty per cent copper which were at first as strongly protective as zinc itself having already so completely lost their surface zinc that they have become electronegative to iron and accelerate its corrosion. All of these alloys have become distinctly red in color. On resurfacing with emery, the original values were obtained. These facts emphasize the point that the protection of a metal by one more electropositive is always at the expense of the latter. Iron under water in contact with zinc will be protected over an area depending on the conductivity of the water so long as the zinc remains: (if a steel sheet with a zinc button riveted to its centre be immersed in water in the presence of air, the radius protected is approximately a straight line with the conductivity of the water, as shown in Plot V. The electrolyte used was KCl.), but iron in contact with a brass will be protected for a very short time, the length of which depends on the per cent of copper, after which its corrosion will be accelerated. The relative periods of protection can be determined from the variation of the depolarizing current with the time, as shown above.

To further show the applicability of the method, the data shown in Plot IV were obtained for the alloys of tin and lead. Terne-plate is claimed to resist corrosion better than tin. These figures prove that lead accelerates the corrosion of iron far more than tin, and that lead-tin alloys accelerate increasingly with the proportion of lead. If terne-plate be really the more resistant, it must be on account either of the smaller number of pin-holes, due to a better adhesion of the coating, or of a different structure of the holes themselves, which interferes with corrosion. It seems more likely that the pin-holes, while fewer in number, corrode more rapidly in terne-plate than in tin. Moreover, the results indicate that, other things equal, the terne-plate containing the least lead necessary to reduce the number of holes to a minimum, will most successfully resist corrosion.

This article has shown the utility of the determination of the depolarizing current as a measure of the influence, under atmospheric conditions, of one metal on the corrosion of another.

This test is of importance in determining the relative effects of various alloys on the corrosion of the iron and steel with which they are to be in contact in construction exposed to moisture.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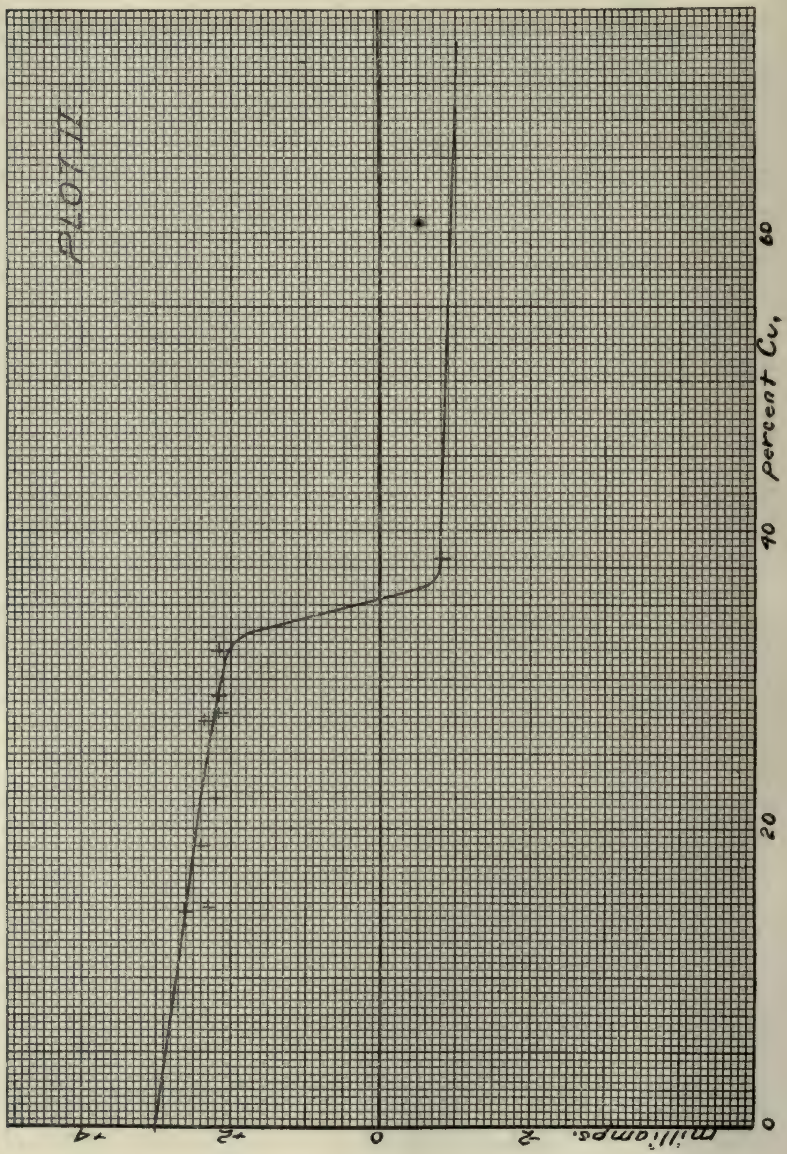
100
150
ccs. per second
1
2
3
milliamps.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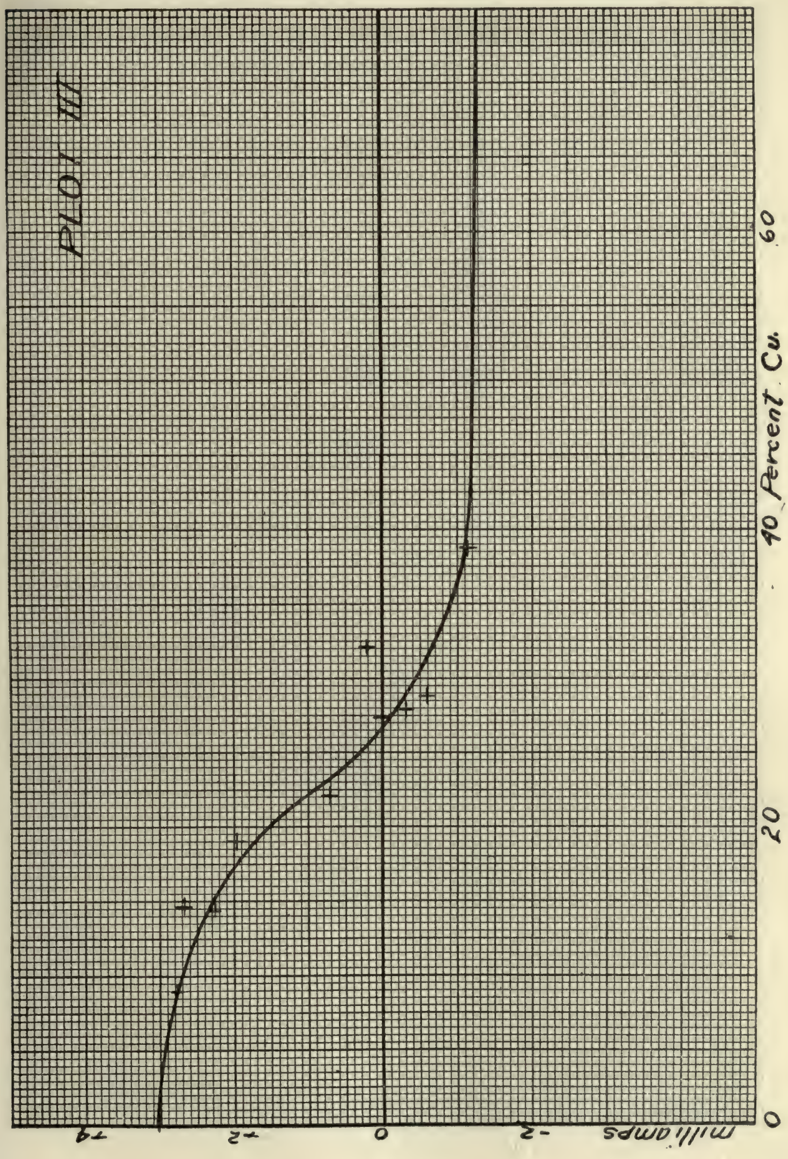
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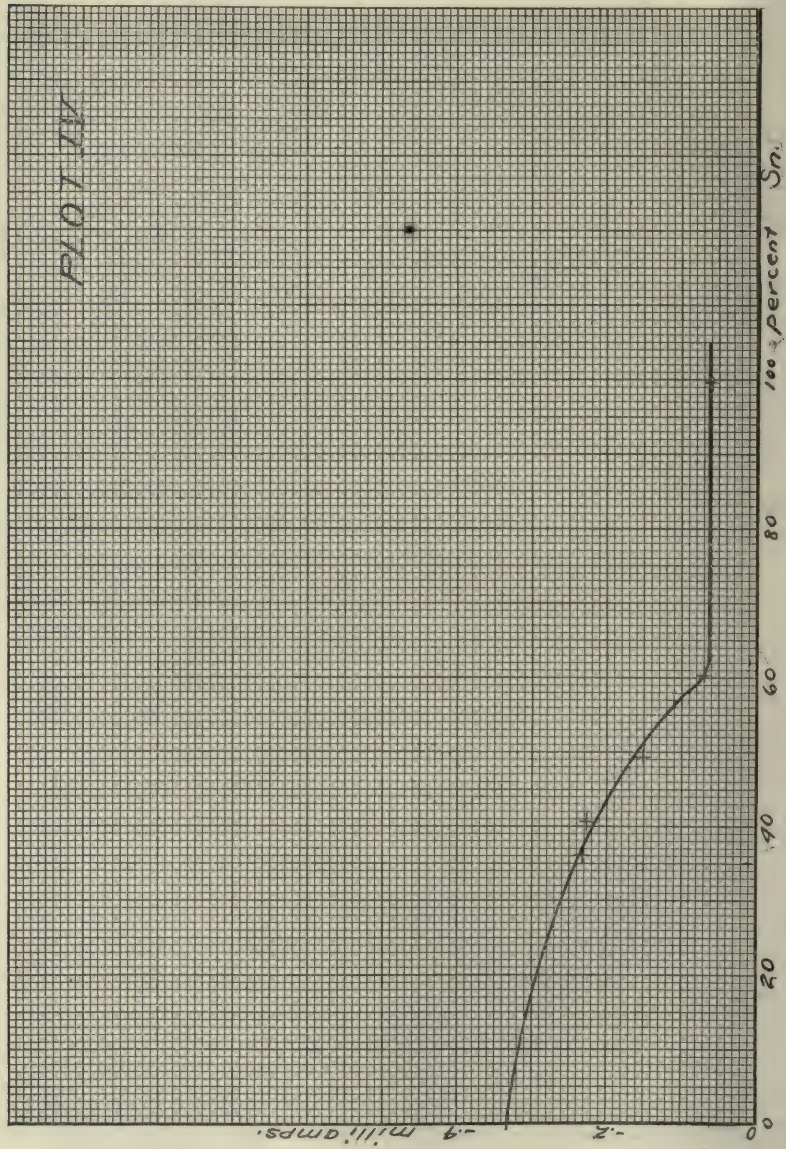
40 Percent Cu.
60
+4
+2
0
-2
milliamps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60
40
20
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0
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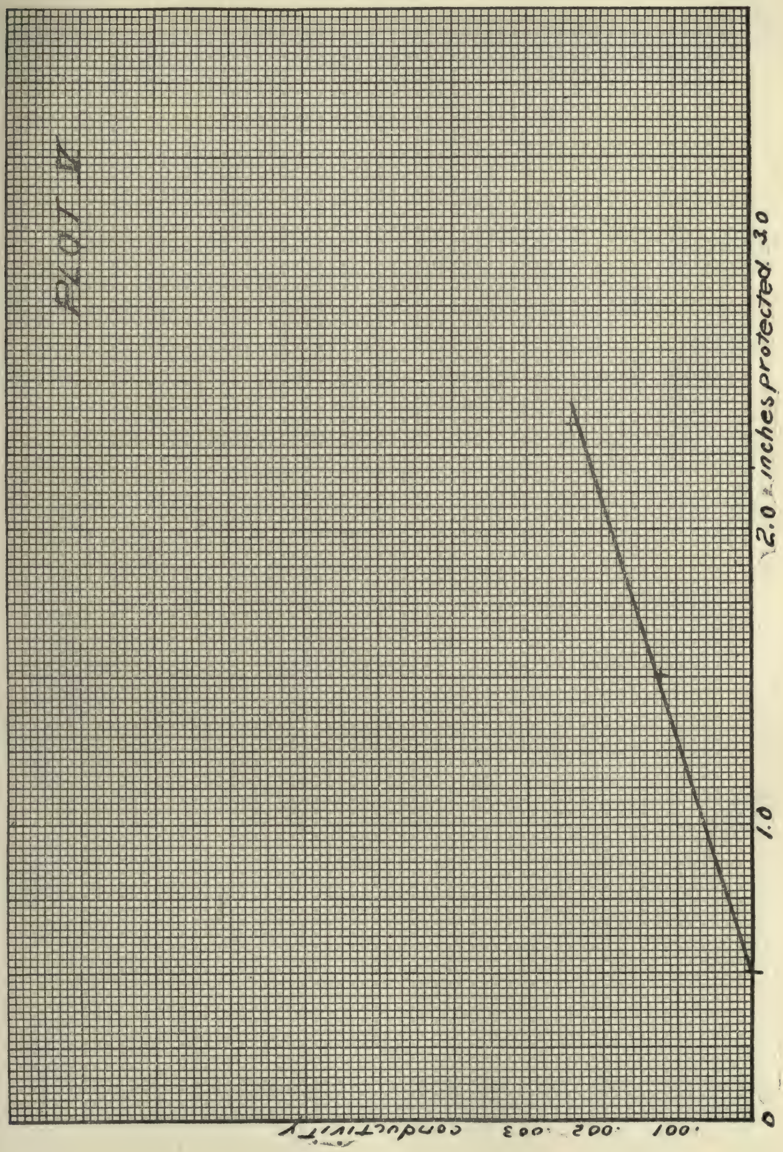
-.4
milli amps.


PLOT V
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1.0
2.0
3.0
inches protected
.001
.002
.003
conductivity

(Abstract)

SIMPLIFYING CALCULATIONS BY THE PROPER CHOICE OF UNITS

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The paper calls attention to the large number of unnecessary numerical calculations now required due to the numerous incommensurate conversion factors which must now be used in calculations in practice because the units at present used bear no simple relations with each other. This is especially the case in calculations involving energy in its different physical forms as for instance in electric furnaces in which chemical and physical processes are produced by energy which is at times chemical, physical, thermal, electrical, mechanical, radiant and luminous; it is always the same energy and yet is expressed in different units, therefore requiring repeated reductions.

It shows how the calculations involved could be greatly simplified by a proper choice of units. The general remedy proposed and urged is to use but one unit for each physical quantity, to make this unit some decimal multiple of the corresponding c.g.s. unit and to select this multiple so as to make the more usual relations of this unit to others unity or a multiple of 10. Practically all of the troublesome conversion factors then disappear by becoming unity. All the electrical units were thus established. This simplicity is at present enjoyed by the physicist in the c.g.s. system and it could be equally well enjoyed in calculations in practice. The already existing practical units of this simple system should be retained. All forms of energy without exception are then stated in watt-hours or kilowatt-hours, and all forms of power in watts or kilowatts which are general units and not specifically electrical. This eliminates the heat units and such conversion factors as the mechanical equivalent of heat or electricity. The new system is simple, easy to understand and use, may be used in part or in conjunction with the older systems and does not necessarily imply a complete abandonment of the older

units. It affords a uniform, international basis to which all physical data can be reduced and in which it can be compared. A table of conversion factors is added for reducing the more important of the older units to those of this simplified system.

Summary. Summarizing briefly, the present paper urges that in general the units used for calculations in practice, should all be made convenient decimal multiples of the corresponding c.g.s. units, hence that there should be only one unit for each physical quantity. This eliminates nearly all the troublesome conversion factors from calculations, thereby greatly simplifying them. Moreover this forms a uniform, international system to which all physical data could to advantage be reduced for direct comparison.

Table

POWER

General:

1 watt = 10,000,000. ergs per second.
1 kilowatt = 1,000. watts.

Mechanical:

1 gram-centimeter per second = 0.000,098,059,7 watt.
1 foot-pound per second = 1.355,73 watts.
1 kilogram-meter per second = 9.805,97 watts.
1 megadyne-meter per second = 10 watts.
1 kilowatt = 100 megadyne-meters, per second.
1 metric horse-power = 0.735,448 kilowatt.
1 horse-power = 0.745,650 kilowatt.
1 (feet fall × cubic feet of water per second) = 0.084,635,7 kilowatt.
1 (meters fall × cubic meters of water per second) = 9.805,97 kilowatts.

Thermal, chemical, physical, etc.:

1 gram-calorie per second = 4.186,17 watts.
1 thermal unit (B.T.U.) per minute = 17.581,6 watts.
1 pound-centigrade heat unit per minute = 31.646,9 watts.
1 kilogram-calorie per minute = 69.769,5 watts.

ENERGY

General:

1 erg = 1 dyne-centimeter.

1 watt-second = 10,000,000. ergs or dyne-centimeters.

1 watt-hour = energy of 10,000,000. ergs per second during one hour.

1 kilowatt-hour = 1000 watt-hours.

Mechanical:

1 gram-centimeter = 980.596,6 ergs.

1 foot-pound = 0.000,376,591 watt-hour.

1 kilogram-meter = 0.002,723,88 watt-hour.

1 megadyne-meter = 10. watt-seconds.

1 (feet fall × cubic feet of water) = 0.023,509,9 watt-hour.

1 (meter fall × cubic meters of water) = 2.723,88 watt-hours.

1 metric horse-power-hour = 735.447 watt-hours.

1 horse-power-hour = 745.650 watt-hours.

Thermal, chemical, physical, etc.:

1 gram calorie = 4.186,17 watt-seconds, or 0.001,162,82 watt hour.

1 thermal unit (B.T.U.) = 0.293,027 watt-hour.

1 pound-centigrade heat unit = 0.527,448 watt-hour.

1 kilogram calorie = 1.162,82 watt-hours.

FORCE

1 dyne = 1.019,79 milligrams.

1 megadyne = 1,000,000 dynes.

1 megadyne = 2.248,25 pounds.

1 megadyne = 1.019,79 kilograms.

1 gram = 980.597 dynes.

1 pound = 0.44,4791 megadyne.

1 kilogram = 0.980,597 megadyne.

1 cubic foot of water (downward force) = 27.7676 megadynes.

1 cubic meter of water (downward force) = 980.597 megadynes.

Pressure

1 barie = 1 dyne per square centimeter.
1 megadyne per sq. cm. = 1 megabarie.
1 megabarie = 1,000,000 baries.

1 gram per square centimeter = 980.597 dynes per sq. cm.
1 millimeter of mercury column = 1,333.21 dynes per sq. cm.
1 foot of water column = 0.029,888,6 megadyne per sq. cm.
1 inch of mercury column = 0.033,863,7 megadyne per sq. cm.
1 pound per square inch = 0.068,942,5 megadyne per sq. cm.
1 meter of water column = 0.098,059,7 megedyne per sq. cm.
1 kilogram per square centimeter = 0.980,597 megadyne per sq. cm.
1 atmosphere (760 mm.) = 1.013,24 megadynes per sq. cm. (megabaries).

Thermal Resistance

Thermal ohms = centigrade degrees ÷ watts = degrees per watt.
1 thermal ohm = a resistance requiring 1° C. per watt of heat flow.
1 thermal ohm = 0.000,000,1 c.g.s. unit of thermal resistance.
1 gram calorie unit = a resistance requiring 1° C. per flow of a gram calorie per second.
1 gram calorie unit = 0.238,882 thermal ohm.
1 c.g.s. unit = a resistance requiring 1° C. per flow of an erg per second.
1 c.g.s. unit = 10,000,000. thermal ohms.

Thermal Resistivity:

1 gram calorie, cm.cb. unit = 0.238,882 thermal ohm, cm.cb. unit.
1 gram calorie, inch cb. unit = 0.606,762 thermal ohm, cm.cb. unit.
1 thermal ohm, inch cb. unit = 2.540,01 thermal ohm, cm.cb. units.

To reduce thermal conductivities to resistivities take their reciprocals.

To reduce thermal conductivities given in B. T. U. per hour, per sq. foot, per inch thickness, per Fah. degree, to thermal ohm, cm.cb. units, multiply the reciprocal of that number by 693.455.

(Note. The above conversion factors are all given uniformly to six places of significant figures in conformity with the rest of those published by the writer. They are of course accurate only in so far as the fundamentals are correct; these are: gravity 980.5966; one kilogram calorie = 426.900 kilogram-meters; one cubic decimeter of water weighs one kilogram; density of mercury 13.595,93; besides the official U. S. Standards.)

RECENT DEVELOPMENTS IN THE ELECTRIC STEEL FURNACE

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New York, N. Y.

The progress of the Electric Furnace for refining steel during the last year has been characterized by a steady improvement in established methods and a reduction in costs rather than by the introduction of any new processes or radical alterations in furnace construction.

The Electric Steel Furnace has now reached a point when the reduction of costs depends entirely on improvements in detail both in furnace construction and manipulation. It may now be said, "that the general principles of electric refining have been so clearly established, that it is now possible to determine those furnaces which are destined to play an important part in the metallurgy of iron and steel."

The growth of the electric process is shown by the following statistics, of the output of electric steel in three countries:—

	1909	1910
Germany	17,773	36,188
Austria-Hungary	9,048	20,028
United States	22,997	55,335

In Europe the process was developed further for high priced steels but in the United States the principal problem has been that of making rails. The present position has been admirably summed up by Mr. W. R. Walker. He stated recently in New York, "that his investigations lead him to believe that the so-called heavy products could be made in the Electric Furnace, in conjunction with the Acid or Basic Bessemer at a cost that would not be prohibitive and that the steel so produced would be exceedingly low in oxygen and other impurities."

He further pointed out, "that his investigations are based on the operation of two fifteen ton furnaces for a period of three years, and on 5600 tons of rails which have been in the track for more than two years under hard conditions of service." He stated, "that although exposed to extreme cold as low as 52° below zero, no breakages have been recorded and that Electric Steel is denser than basic and open-hearth and Bessemer Steel and that no oxides or slag enclosures can be detected at a magnification of 1000 diameters." He further pointed out, "that Electric Steel can be made with smaller additions of manganese and that equal wearing properties can be obtained from an Electric Steel containing about .08% less carbon than a similar open-hearth steel, thus reducing the risk of breakage, without sacrificing wearing qualities."

At the present time the application of the Electric Furnace for the manufacture of intermediate steel, and all qualities of alloy and special steels is established; and the application of the Electric Furnace for these purposes has been so clearly proved successful that it is only a question of time before the general application of the process will become not only advantageous but absolutely necessary to compete in this class of trade.

The quality of castings made in the Electric Furnace, especially for automobiles and for all kinds of machine parts is superior to that made by any other process; while the cost of steel refined by electricity as compared with that made by the Crucible process is so much lower that it enables castings of Crucible steel quality to be made at a price about the same as those made from the highest quality acid open-hearth steel. The importance of this can not be over estimated in the machine shop, for it often happens that several hundred dollars worth of machine work will be put into a casting before the blow holes and other defects can be detected. By the use of the Electric Furnace the quantity of blow holes and wasters can be reduced to a minimum and saving in the cost of machine work alone would justify paying a very much higher price for electric steel castings, if this were necessary.

In the case of many low carbon high quality castings made in the Electric Furnace, it is unnecessary to anneal them and this makes an additional saving in the cost of manufacture.

The following tests were given by ordinary mild steel castings from an Electric Furnace:—

ELECTRIC STEEL CASTINGS

Analysis

Carbon .12 Mn. .40 Si. .20 Sul. & Phos. below .02.

Test No.	Area Sq. In.	Reduction of Area	Elastic Limit per Sq. In.	Ultimate Strength per Sq. In.	Elongation Dia. ½″
36138	.2454	39.5%	45,696 lbs.	71,456 lbs.	3″—28.75%
36139	.2359	53.2%	33,376 "	63,616 "	3″—35.00% 2″—34.00%

From these figures it will be seen that it is possible to make a mild steel casting comparing favorably with plate steel, and the question arises whether the working of steel under the hammer or rolling mill can improve its quality in any way whatever if the steel be free from faults and cavities.

Another application of the Electric Furnace which is of great importance to manufacturers of alloy steel depends upon the fact that any quality of scrap can be worked up and the valuable metals retained. Thus, for example: It is not uncommon practice to melt up charges of miscellaneous Tungsten steel including various tools, turnings, hammer scale and "spillings" from Crucibles, all of which contain a certain quality of Tungsten. Such a charge can be melted up, and the necessary additions made to bring the composition up to the required specification.

Another case of this kind is the manufacture of chrome nickel and vanadium steels for automobile work, etc., from miscellaneous scrap containing unknown quantities of nickel and chrome and vanadium. Such scrap is often sold at a low price owing to the loss in remelting by ordinary methods and on account of the very large percentage of scrap in ornament and other works, where government specifications and other causes excessive scrap production. It is not uncommon to melt up such a miscellaneous charge and take bath samples, make the necessary analysis in forty minutes, and add the necessary alloys for the steel required.

With regard to the reduction in cost, which has been effected during the last few years, it may be said that this is almost entirely due to slight improvements in practice and design which are the results of continuous experience. Two years ago it was considered good practice to melt and refine steel scrap in six hours at a power consumption of 750 K. W. Hrs. per ton, whereas, at present furnaces are working steadily carrying out the same operation in four hours at a power consumption of under 600 K. W. Hrs. over periods of six months. Similar reductions in operating expenses have been made in all other details, such as: labor charges, refractories, etc.

With reference to the question of refining large tonnages of steel, a great deal of work has been done during the last two years but the conditions are more complicated and the economical questions have to be considered with great care in each special case. Thus for instance: In Germany where 95% of the output of steel is made by some basic process and the ores are such that they are entirely dependent upon the basic bessemer process for the cheap production of steel, the application of the Electric Furnace will be found in the refining of steel which has previously been treated by the basic bessemer process. Steel made by this process is not sufficiently uniformly reliable to meet the requirements of modern engineering, and the German steel makers find themselves faced with the necessity of abandoning the basic bessemer process on which they are dependent for cheap steel or of adding electric refining to their present process. Several furnaces have been operated in this way for the last twelve months and the results are so satisfactory that furnaces of 25 tons capacity have just been put into operation to work as conjunction with basic converters of the same capacity. In this way a steel superior to the basic open-hearth product will be made at a cost which will probably be not much greater after the furnace has been running for twelve months and the plant is brought up to full capacity.

The progress of electric steel refining has been retarded considerably by the large number of unsuccessful furnaces that have been erected by men who possess no special knowledge of electric furnace work or the steel trade and considerable quantities of inferior steel have been turned out in the past as a result of this. To erect and operate an electric furnace successfully it is essential to have had considerable experience, both in the steel trade in general and in electric furnace work in particular, as the old established principles of steel making cannot always be followed. As progress continues and operating expenses are reduced, a continually widening field for the process and a cheapening of the best qualities of steel will result together with an improvement of the quality of castings and other materials which can be manufactured at a low price.

Time has also eliminated many difficulties and fallacies relating to electric furnace work, so that it is now easier for the steel maker to decide the type of furnace he should adopt and to undertake the manufacture of electric steel with complete confidence.

THE SYNTHESIS OF HYDROCARBONS AT HIGH TEMPERATURES AND PRESSURES

By J. N. Pring, D.Sc. and D. M. Fairlie, M.Sc.

Manchester, England

A systematic study of a number of chemical reactions at high gaseous pressures, in a specially constructed electric furnace, was first carried out by Hutton and Petavel (Phil. Trans. London, 1908, A. 207, 428). Such reactions were studied as the formation of calcium carbide, silicon carbide, the reduction of alumina by carbon, the fusion of silica, and the synthesis of oxides of nitrogen. Temperatures up to about 3000° C were used and pressures up to 200 atmospheres.

The present paper deals with a detailed investigation which has been conducted by the authors, on the synthesis of hydrocarbons at high temperatures and pressures. The apparatus constructed for this work is a modified form of the pressure furnace used by Hutton and Petavel.

The investigation, which was carried out at temperatures and pressures which were carefully measured and controlled was directed mainly to the determination of the quantities of methane which are in equilibrium with carbon and hydrogen at different temperatures. In this way it has been possible to obtain data which will correlate the values for the specific heats of hydrogen, methane, and different forms of carbon at high temperatures. The influence of temperature on the displacement of the equilibrium constant of a chemical reaction is a function of the heat change which accompanies the reaction at that particular temperature, while the heat of reaction itself changes with the temperature according to the specific heats of the substances taking part in the equilibrium.

The dependence of a chemical equilibrium, on the various heat changes involved in the reaction has been pointed out by van't Hoff, and further developed by Nernst and Haber, but there are very few cases where sufficiently accurate data are available to verify the application of these formulae at high temperatures.

In all cases when substances in a condensed system interact chemically, the reaction proceeds until a certain equilibrium stage is reached, when further action ceases, though in many cases the equilibrium stage is so far developed in one direction that the reaction appears to be complete.

At low temperatures equilibrium values are often of very little importance, since under these conditions the rate of chemical reaction is usually so slow that the equilibrium value is never reached and does not come into question. At high temperatures, however, the conditions are usually quite different, the final equilibrium stage being more quickly reached, so that usually chemical changes do not complete themselves, but proceed to a certain stage, at which point the same proportion between the substances taking part, and the products of the reaction is obtained from whichever side the equilibrium is approached. At low temperatures, many substances are in an unstable or "metastable" condition though they undergo no apparent change on standing, but at high temperatures this is not possible as the change into the stable form proceeds with a velocity which continually increases with the temperature.

The reactions which have been investigated in this work, viz. the synthesis of hydrocarbons, involve a case of the interaction of a solid with a gas. In the case of each hydrocarbon a certain equilibrium stage is reached when the particular hydrocarbon bears a definite ratio to the quantity of hydrogen present. The quantity of carbon does not come into consideration in this equilibrium, since its active mass does not vary under different conditions.

As methane is an exothermic compound, it follows that the equilibrium amount decreases with increase of temperature. Below 1000°, carbon and hydrogen at atmospheric pressure unite so slowly, even when the former is in presence of a catalyst like platinum, that equilibrium in the yield of methane cannot be reached in any reasonable time.

The velocity is considerably increased at high pressures, but even in this case it was not found practicable to determine the equilibrium value with methane below about 1100°.

Above this temperature, this synthesis was measured by heating carbon in the form of a rod in presence of hydrogen. The heating was effected by the passage of an electric current through the rod, which was thus the only part of the apparatus to be heated. The containing walls of the steel vessel were cooled by water.

Since methane is stable in larger amounts the lower the temperature, it follows that the quantity of this hydrocarbon finally yielded will correspond to the equilibrium at the temperature of the heated carbon, since no decomposition could occur in passing to the colder regions of the apparatus. A large amount of work has been carried out by the present authors[1] on the synthesis of hydrocarbons at atmospheric pressure and it has been found that traces of ethylene are also formed at 1300° and above, but the quantity does not reach any considerable magnitude below 1500° (at 1400° the quantity in equilibrium at atmospheric pressure is about 0.005 per cent.).

The ethylene will react rapidly with the hydrogen in the cooler parts of the vessel, giving methane and thus gradually raising the quantity of the latter above the equilibrium value at the high temperature. However in the short time necessary to produce equilibrium with methane in these experiments at high pressures it was calculated that this disturbance would not reach any appreciable magnitude when working below 1500°.

With regard to the synthesis of acetylene, it was found in the earlier work cited above that this first becomes noticeable (about 0.001%) at 1650°, and the amount produced increases with the temperature, in accordance with the fact of its being an endothermic compound.

However it has not been possible to determine the precise equilibrium values with acetylene, on account of the non-uniform temperature of the interior of the reaction vessel, which causes decomposition of the gas produced at the high temperature of the carbon to take place in regions of lower temperature. Moreover at temperatures where the quantity of acetylene attains any considerable magnitude an exact estimation of the methane equilibrium is no longer possible, on account of the rapid polymerisation of the acetylene with hydrogen, giving methane in the cooler parts of the vessel. For this reason, it has only been found possible in this work to measure with any accuracy the equilibrium with methane, and that only in the range of temperature between 1100° and 1600°, though the experiments were extended up to 2100°. It has been shown moreover that in this range, and at pressures up to 200 atms. no hydrocarbons other than methane, ethylene, and acetylene can be formed or can exist in any detectable quantity.

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[1] Pring and Hutton, Trans. Chem. Soc. (London), 1906, *89*, 1591. Pring, *ibid.* 1910, *97*, 498. Pring and Fairlie, *ibid.*, 1911, *99*, 1796; 1912, *101*, 91.

Considering the synthesis of methane, since the equilibrium is expressed by the equation $C+2H_2=CH_4$ it follows in accordance with the law of mass action that $\frac{p.CH_4}{p(H_2)^2}=K$ or the concentration of methane divided by the square of that of the hydrogen is a constant at any particular temperature. It follows from this that an increase in the pressure of n times will increase the ratio of methane to hydrogen n times.

A proof that definite equilibrium values are obtained lies in the fact of the same final quantity of methane resulting in whichever direction the reaction is made to proceed, and further by the same value being obtained for K, the equilibrium constant, whatever gaseous pressures were employed.

Description of Apparatus

The pressure cylinder (V) (Fig. 1.) was forged from a piece of nickel steel of high tensile strength. The steel tubes E.E. which served to lead in the current were cooled by water circulation, and contact with the carbon was made by means of nickel clamps (N.N.), which were brazed to the ends of these leads. The arrangement in the diagram shows provision for heating wider carbon tubes in which crucibles can be placed, but for the present purpose, tubes or rods of carbon longer and narrower than the one shown in the diagram were used. These rods or tubes (C) were always fitted in graphite end pieces which were held in the nickel clamps. The steel tubes emerged from the furnace at the stuffing boxes P.P. and were insulated from the walls by means of small tubes of ebonite or fibre (F.F.). Asbestos cord mixed with a little tallow was used as the packing material for the boxes (P.P.), and was compressed by the brass rings R.R. which were forced down on to the ebonite tubes by 6 bolts, as at K.K. The outward thrust of the electrodes was secured by the bolts T.T. of which there were two at each end of the furnace. The top part of the furnace was fastened down by 6 bolts as at B.B. and a gas tight joint made by means of the lead spigot S.S. By opening the bottom stuffing box and removing the packing, the bottom electrode could be lifted while clamped to the carbon rod which was also held in the top electrode. The two electrodes and the carbon tube could thus be all lowered into position together with the furnace top, and afterwards raised in the same manner. Water circulation was provided in the annular jacket M. The gas was admitted through the valve V. and the pressure read directly on a gauge. The glass window W. was placed at a sufficient distance to be protected from the heat of the carbon. Temperature readings were taken by means of a Wanner optical pyrometer, from the light radiated from the carbon, after passing through the window and being reflected from a mirror placed in front at an angle of 45°. By comparing the optical readings in the case of graphite with those given at the same time by a thermojunction, it has been found that there was no appreciable departure at 1300°, so that graphite must radiate approximately like the theoretical "black body." Measurements were made from time to time of the error arising from the absorption of the window and mirror. At 1400°, this usually amounted to about 60°. The absorption at any other temperature can be calculated from the formula $\frac{1}{T_1}=\frac{1}{T_2}-C.$ where T_1 is the real, T_2 the apparent temperature after absorption, and C. is a constant for any given sample of glass.[1]

The window could as a rule be safely used with pressures up to 200 atms. and the remainder of the furnace was capable of withstanding a pressure of 1000 atms.

The carbon used at C. consisted in some cases of the amorphous retort variety in the form of tubes 12 cms. long and either 20 mms. external and 15 mms. internal, or 15 mms. external and 9 mms. internal diameter.

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[1] Pring, Lab. Exercises in Phys. Chemistry, page 151. Manchester University Press.

With the smaller size, a current of 500 amps. at 27 volts, would raise the temperature to 1600°, when using hydrogen at 150 atms. pressure.

In other experiments, rods of (Acheson) graphite 12 cm. long and 9 mm. diam. were used.

In the case of amorphous carbon when given no preliminary purification, after mounting in the furnace, a partial purification was obtained by heating to about 1400° in hydrogen at about 50 atms. pressure, and then liberating and renewing the gas.

The quantity of combined hydrogen present as impurity in the carbon was always well below the amount of methane subsequently synthesised. The capacity of the furnace was about 750 c. c. A number of experiments at lower pressures were carried out with rods of amorphous carbon, 5 to 7 mm. diam. and 12 cm. long, which had been carefully purified by heating electrically in chlorine in a glass vessel to about 1500° for a few hours, and then in hydrogen in the same manner.

On account of the corrosion of the carbon, it was not as a rule possible to use the same rod or tube in more than one experiment. In the course of a large amount of work where carbon rods and tubes have been heated at atmospheric pressure under different conditions, it has been found that the heating, in the case of amorphous carbon, always takes place with great uniformity throughout the whole length and up to the cooled points of support. This is due to the negative temperature coefficient of resistance which causes a greater expenditure of electrical energy in places which tend to become cooler. With graphite however the temperature falls near the cold ends of support.

Preparation of Materials

Hydrogen. Electrolytic hydrogen was obtained commercially in steel bottles at a pressure of 120 atms. On analysis, it was found to contain 0.2 per cent of nitrogen, and no appreciable quantity of other impurity. After admitting the gas to the furnace, the heating of the carbon enabled the pressure to be raised to 200 atms.

Carbon. Different varieties of carbon were used as explained above, and in some cases, were first purified by heating to a high temperature in an atmosphere of chlorine.

In some experiments the carbon was used in presence of platinum or palladium, to act as a catalyst. For this purpose, a layer of the metal was obtained by electrodeposition from a chloride solution.

Methane. In some experiments an atmosphere of methane was admitted to the previously evacuated furnace, before filling in the hydrogen at high pressure. The hydrocarbon for this purpose was prepared by decomposing commercial aluminium carbide with water, washing the gas with ammoniacal cuprous chloride to remove acetylene and hydrogen sulphide, and then liquefying by means of liquid air. After evaporation, the gas was collected over water in a large holder of 20 litres capacity.

Analysis of Gases

The gas obtained in these experiments, which contained from 1 to 20 per cent methane, was analyzed in the Sodeau apparatus. By shaking the gas with an ammoniacal silver nitrate solution, acetylene (if present) was completely, and ethylene, partly absorbed. The remainder of the ethylene could then be removed by means of bromine. Carbon monoxide was then taken out by shaking with a freshly prepared solution of ammoniacal cuprous chloride. The hydrogen was then removed by mixing with an excess of oxygen and passing a few times over palladium sponge maintained at about 80° in a water bath.[1]

The saturated hydrocarbon could then be identified and estimated by the relation found between the contraction after combustion with oxygen, and the volume of carbon dioxide formed, as ascertained by absorption with potassium hydrate solution. In all these cases, methane was at all temperatures found to be the only saturated hydrocarbon produced.

In an experiment carried out at 1275°, an examination was made for traces of ethylene by circulating a large quantity of the gas (25 litres) through a tube cooled in liquid air. Most of the methane was thus condensed, together with practically the whole of any ethylene present, as the latter has a higher boiling point than methane. This liquid was then allowed to evaporate slowly, and the last portion was passed through a tube containing carefully purified cocoanut charcoal, which had previously been heated for some time at a red heat in a high vacuum. The gas absorbed by the charcoal in this experiment was then removed in fractions by evacuating. The last portion of 50 c.c. was analyzed and found to contain 0.51 c.c. of ethylene or 0.002 per cent of the total gas, while the amount of methane in this particular sample was 21 per cent. The ratio of ethylene to methane is lower than that found in earlier work at atmospheric pressure, and the ratio of ethylene to hydrogen is higher. This result is in agreement with the effect which would be expected theoretically from the influence of pressure on the yield of the different hydrocarbons.

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[1] Compare Pring and Fairlie, Trans. Chem. Soc. (London), 1911, *99*, 1796.

Change of Pressure

The formation of methane, proceeding according to the equation $C+2H_2=CH_4$ is accompanied by a contraction of volume equivalent to the volume of methane formed. In these experiments at constant volume this was equivalent to a change of pressure.

Consequently by reading the pressure indicated by the gauge, the course of the reaction could usually be followed, and the attainment of equilibrium recognized. However a considerable time was usually necessary for the mean temperature of the enclosure to become constant on account of the large quantity of metal present. Samples of gas were usually withdrawn at two or more different periods during the experiment, in order to ascertain when equilibrium had been reached.

The results of all experiments which were completed are tabulated below according to the particular variety of carbon, and in order of temperature.

As follows from the unstable nature of amorphous carbon, it was found that this modification gradually changed into graphite during the experiments in which it was heated at temperatures above 1100°, in presence of hydrogen. This change took place more rapidly the higher the temperature. It was found that the amorphous carbon which had been purified by heating to a high temperature in chlorine and then in hydrogen was always more or less graphitised.

Amorphous carbon was found to give a considerably higher percentage of methane than graphite, and on beginning an experiment with amorphous carbon, the yield of methane which was at first obtained gradually fell concomitantly with the change of amorphous carbon into graphite. The increased yield of methane with amorphous carbon is in excess of the stable equilibrium value, and thus denotes a false or metastable equilibrium. This is only possible to such a degree on account of the great inertness of methane, or the slow rate at which it breaks down into carbon and hydrogen.

These false equilibrium values with amorphous carbon have also been noticed by Schenck and Heller [1] who studied the equilibrium in some reactions in which carbon in different modifications takes part.

In the case of the equilibrium between carbon dioxide, carbon monoxide, and carbon, the reduction of the first was greatest when amorphous carbon was used.

A similar result was obtained in the reaction between iron oxide, and carbon, thus in this case, at 550°, the pressure of the latter when in "metastable" equilibrium was, with amorphous carbon, 59 mms.; diamond, 22 mms.; and the stable equilibrium value with graphite was 12 mms.

In the present work the results with amorphous carbon are given in Table I. below. In some cases, the carbon was impure (though containing less total hydrogen than the quantity of methane subsequently formed); in others, the substance was partly purified in chlorine at a temperature too low to cause any appreciable change into graphite. In all cases the results in this table refer to carbon which was used for the first time. In Table II. are given the experiments done with graphite. This was either Acheson graphite or else carbon which had been used in a previous experiment and heated for a long interval at a high temperature in hydrogen, or else it had been purified at a high temperature in chlorine so as to cause transformation into graphite. The carbon in all these cases was practically pure.

In Table III. are given the experiments with carbon which by previous heating or purification, had become partly transformed into graphite. In some cases a thin layer of platinum or palladium was coated on to the carbon by electrodeposition as explained above to serve as a catalyst. These cases are pointed out in the first column of the tables.

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[1] Ber. 1905, *38*, 2139.

The general results are also plotted in the form of curves (Fig. 3.), where the ordinates denote the equilibrium constants and the abscissae the temperatures. The only values which are quite definite are those obtained with graphite. In the case of amorphous carbon, a continuous change in the methane yield followed the graphitisation of the carbon. The whole of the results are entered in Fig. 2. though a number of the experiments in the case of graphite were not quite taken to the equilibrium point, so that the curve has been drawn through the maximum values.

TABLE I

Amorphous Carbon. First Time of Use

Nature of carbon	Temperature	Time	Pressure (atms)	Percentage composition				$K = \frac{p\text{-}CH_4}{p\text{-}(H_2)^2}$
				CO	CH_4	C_2H_2	C_2H_4	
Purified Pt. coated....	1100°	0	—	—	4.10	—	—	—
		2½ hrs.	20	1.1	6.35	—	—	0.00390
Impure. Pt. coated....	1220	0 "	—	—	4.1	—	—	—
		3 "	18	1.4	5.6	—	—	0.00376
Partly purified........	1275	3 "	100	0.25	21.5	—	0.002	0.00359
Impure. Pt. coated....	1350	1 hr.	166	0.6	18.5	—	—	0.00173
		2½ hrs.	153	0.7	20.9	—	—	0.00224
Purified. Pt. coated....	1400	0	—	—	4.35	—	—	—
		1¾ "	18	0.92	3.86	—	—	0.00245
Same carbon as above..								
(To show effect of progressive graphitisation)	1400	1½ "	19	1.0	2.35	—	—	0.00138
		3 "	18.5	1.4	1.98	—	—	0.00120
		4½ "	17.5	3.3	1.28	—	—	0.00084
Impure..............	1550	0	—	—	4.65	—	—	—
		1½ "	21	1.5	3.49	—	—	0.00188
"	1620	20 mins.	20	3.7	1.0	—	—	0.00058
" Pt. coated.....	1700	1 hr.	15	7.5	1.4	nil	—	0.00120
"	1775	4 hrs.	117	1.6	9.0	nil	0.1	—
"	1950	7 mins.	24.5	3.4	2.4	0.29	0.44	—
"	2050	7 "	23	2.8	2.8	0.74	1.10	—
Purified..............	2100	0	—	—	5.5	—	—	—
		15 "	25	5.5	2.6	0.25	?	—

The values obtained in experiments above about 1700° do not represent equilibrium quantities, as the methane in these cases is formed chiefly by the reaction of ethylene and acetylene with hydrogen in the cooler parts of the vessel. The results at these higher temperatures are consequently not plotted in the figure.

TABLE II

Graphite

Nature of graphite	Temperature	Time	Pressure (atms)	Percentage composition of gas		$K = \frac{p\text{-}CH_4}{p\text{-}(H_2)^2}$
				CO	CH_4	
Acheson	1200°	2½ hrs.	105	0.0	17.5	0.00244
Carbon graphitised by heating. Pt. coated	1275	0	—	—	2.38	—
		25 mins.	37	1.6	4.23	0.00133
		1¾ hrs.	32	2.4	4.02	0.00147
Carbon graphitised by heating. Pd. coated.	1300	½ hr.	37	0.6	4.69	0.00120
		1 "	35.5	1.0	4.55	0.00146
Acheson	1300	1 "	117	0.0	11.2	0.00126
		2¼ hrs.	106	0.0	12.6	0.00158
Carbon graphitised by heating	1375	1 hr.	28	1.4	2.5	0.00100
Acheson	1375	3 hrs.	115	0.2	10.6	0.00117
Graphitised by heating. Pd. coated	1400	0	—	—	2.4	—
		¼ hr.	46	0.1	3.90	0.000945
		1¼ hrs.	46	0.2	4.29	0.00103
Graphitised by heating. Pt. coated	1400	0	—	—	1.6	—
		1½ "	50	1.3	3.99	0.00089
Same carbon as above	1400	0	—	—	1.6	—
		¾ hr.	55	0.5	4.24	0.00080
		1¾ hrs.	48	1.0	3.71	0.00089
Carbon graphitised by heating. Pt. coated.	1450	0	—	—	2.3	—
		20 mins.	47	2.0	3.39	0.000843
		1 hr.	44	2.4	3.01	0.000746
Carbon graphitised by heating. Pt. coated.	1500	0	—	—	1.8	—
		½ "	55	0.8	3.96	0.00080
		1 "	52	1.2	3.62	0.00077
Carbon graphitised by heating. Pt. coated.	1575	0	—	—	—	—
		12 mins.	52	0.7	2.94	0.00063
		1½ hrs.	44	1.0	2.46	0.00062

Results and Conclusions

The reaction between carbon and hydrogen resulting in the formation of methane was found to proceed with increased velocity at high gaseous pressures. Using carbon in the form of a compact rod or tube, and either in presence or absence of a cataylst, the equilibrium stage was reached in about 2 hours, when the temperature was 1200° to 1300°, and the pressure 30 to 50 atms. Above 1400°, equilibrium was reached in about 15 mins.

under the same conditions. At 200 atms. the reaction was still more rapid.

TABLE III

Partly Graphitised Carbon

Nature of carbon	Temperature	Time	Pressure (atms)	Percentage composition of gas		$K = \frac{p\text{-}CH_4}{p\text{-}(H_2)^2}$
				CO	CH_4	
Purified	1300°	$1\frac{3}{4}$ hrs.	7	7.3	1.0	0.00178
Impure. Pt. coated	1350	2 "	11.5	5.75	1.71	0.00178
Purified "	1450	$1\frac{1}{4}$ "	136	0.3	17.1	0.00186
Impure. "	1475	$1\frac{1}{4}$ "	177	0.3	16.7	0.00137
		$4\frac{1}{2}$ "	155	0.3	11.9	0.00101
Impure	1475	$1\frac{1}{4}$ "	200	0.05	13.1	0.00087
		$3\frac{1}{4}$ "	200	0.25	12.4	0.00083
Impure	1540	$1\frac{1}{2}$ "	183	0.05	12.0	0.000860

The results indicate the probability that carbon in a fine state of division would at still higher pressures combine with hydrogen with extreme rapidity, as the action is exothermic. In this way the preparation of methane, though necessarily present with a small percentage of hydrogen, might most conveniently be carried out on a large scale.

The relative amount of methane produced increases with the pressure to the extent demanded by the law of mass action as applied to the reaction $C+2H_2=CH_4$. According to this the value of $\frac{p.\,(CH_4)}{p.\,(H_2)^2}$ should be constant at any given temperature.

In all experiments, at pressures varying from 10 to 200 atms. a value which was constant within the limits of experimental error was always obtained for this ratio at any particular temperature, and when the same modification of carbon was used. In some experiments, where an amount of methane in excess of this value was added to the gas beforehand, decomposition took place until the same final value was obtained. Consequently this represents the true equilibrium constant.

The amount of methane which at atmospheric pressure is in equilibrium with hydrogen and graphite is at 1200° equal to 0.24 per cent, and at 1500°, 0.07 per cent. For amorphous carbon, the "metastable" equilibrium values are 0.36 per cent at 1200°

and 0.18 per cent at 1500°. At a pressure of n atmospheres, the ratio of methane is n times as great as at 1 atmosphere.

The values found in this work for the equilibrium constants in the case of carbon and graphite enable an approximate calculation to be made of the heat of reaction in the transformation of amorphous carbon into graphite. According to Berthelot[1] at ordinary temperatures, this has the value 2840 cals. per gram atom. This value at first falls with increase of temperature and at some temperature below 1000° becomes zero. Consequently amorphous carbon is the stable form at this temperature, but not at ordinary temperatures. When heated above this stable point, it again becomes unstable, and consequently passes more or less rapidly into graphite with evolution of heat.

The heat evolved in this transformation at different temperatures can be calculated by means of a formula deduced by van't Hoff. In this $Q_{(t)} = RT \ln . \frac{K_{(1)}}{K_{(2)}}$.

Where $Q_{(t)}$ is the heat of reaction at the absolute temperature T . R, the gas constant in calories (1.98) . $K_{(1)}$. the equilibrium constant in the methane formula with amorphous carbon, and $K_{(2)}$ that with graphite. We have from the above results, the following values for the heat of reaction at different temperatures.

Temp. Centigrade	Temp. absolute	$K_{(1)}$	$K_{(2)}$	$Q_{(T)} = RT\ln\frac{K_1}{K_2}$
1200°	1473	0.004	0.00245	1480
1300°	1573	0.003	0.0016	1950
1400°	1673	0.0023	0.0011	2450
1550°	1823	0.0017	0.0007	3200

It has been shown by Kirchhoff that the heat of a chemical reaction changes with the temperature in the following manner:—

$$Q_{(t)} = Q_{(0)} + T(c_{(f)} - c_{(p)})$$

where $c_{(f)}$ is the mean specific heat of the factors (in this case carbon), and $c_{(p)}$ that of the products of the reaction (in this case graphite).

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[1] Compt. rendu. 1889, *108*, 1144.

Since Q. increases with the temperature it follows that the mean specific heat of carbon at temperatures above 1100° is higher than that of graphite, and the difference increases rapidly with the temperature.

The values given by Kunz [1] for carbon and by Weber [1] for graphite show the opposite relation at all temperatures above 200, and are consequently not applicable at these high temperatures.

It would indeed follow from the values of Kunz and of Weber that amorphous carbon would be stable at all temperatures.

It was also found that no saturated hydrocarbon other than methane is produced or is stable at any temperature or pressure employed in this work.

[1] Ann. Physik. 1904 iv, *14*, 327. Ber. 1872, *5*, 303.

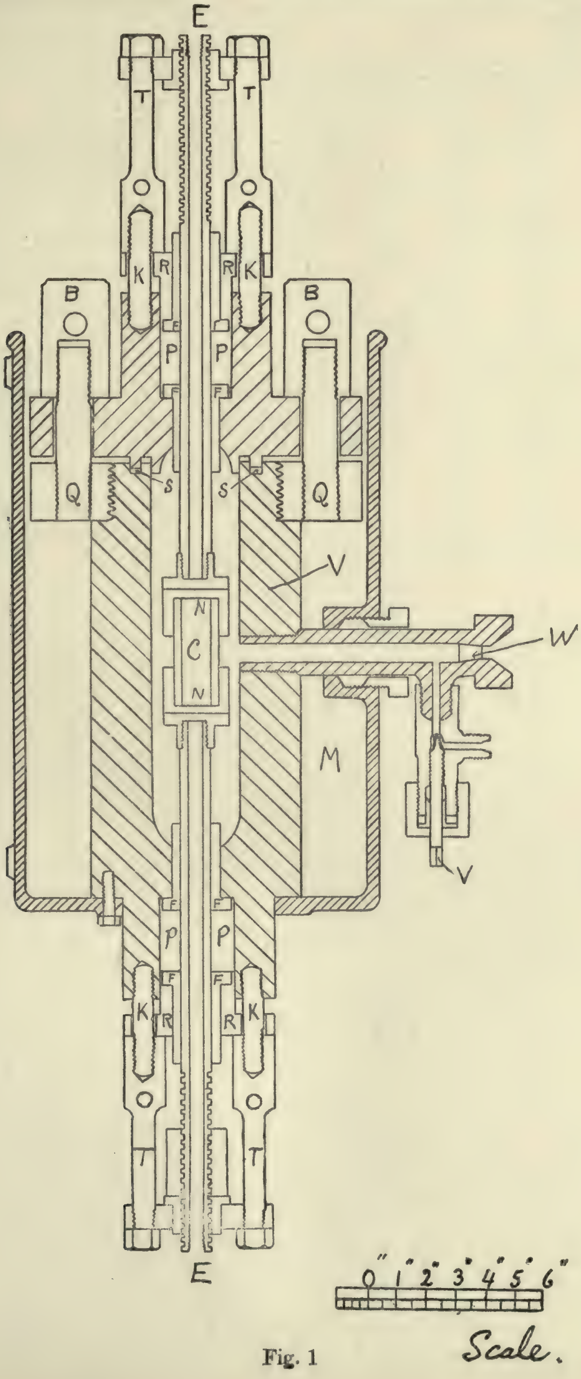


Fig. 1

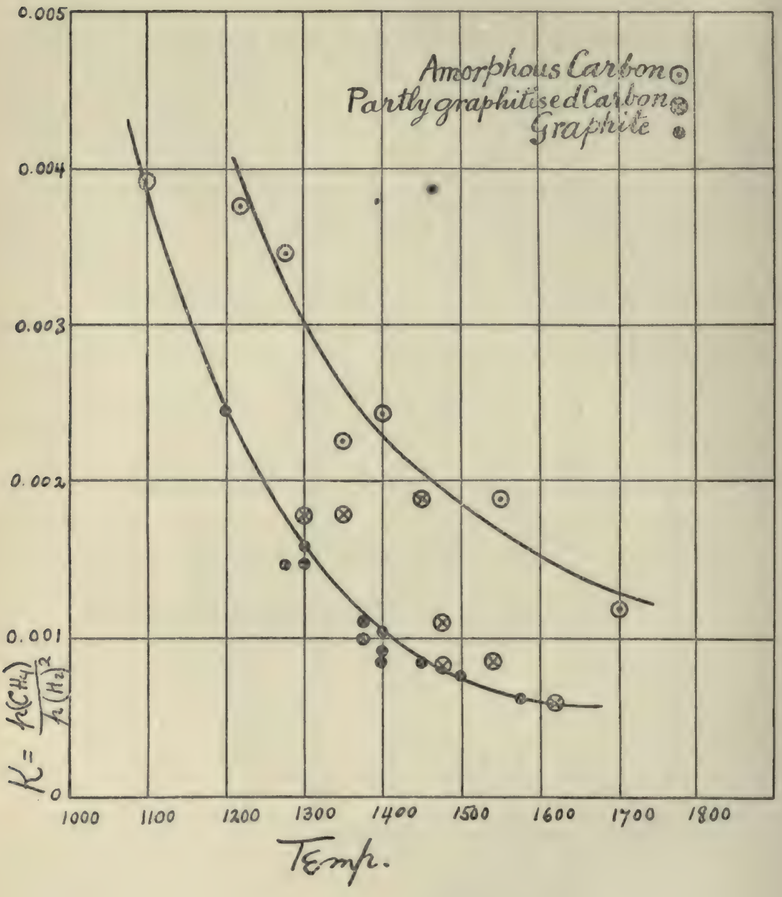
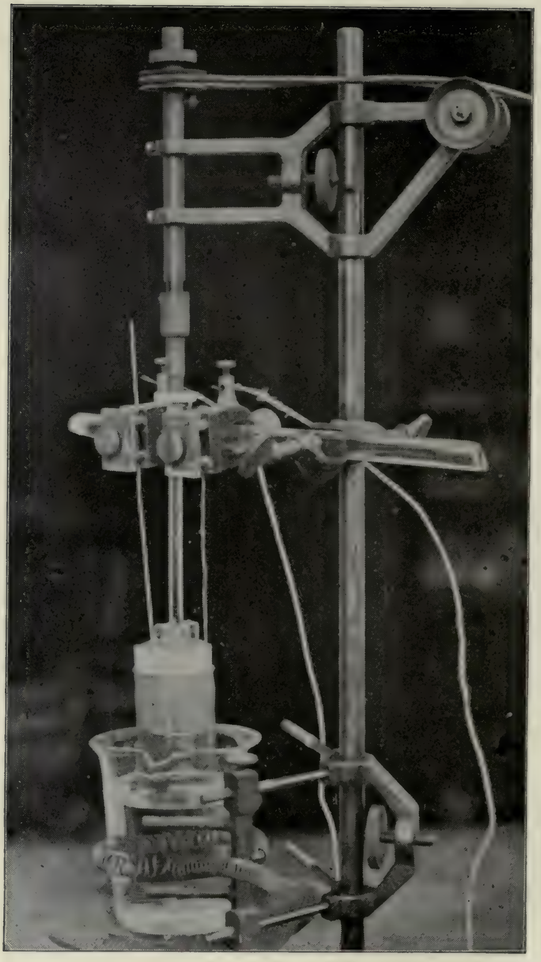

Amorphous Carbon ⊙
Partly graphitised Carbon ⊗
Graphite ●
0.005
0.004
0.003
0.002
0.001
0
$K = \frac{p(CH_4)}{p(H_2)^2}$
1000
1100
1200
1300
1400
1500
1600
1700
1800
Temp.

Fig 2



Picture showing method of clamping the Sand-Fischer electrodes

THE ELECTRO-ANALYSIS OF COPPER, ANTIMONY, BISMUTH AND TIN WITH ACIDIFIED CHLORIDE ELECTROLYTES.

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Solutions of chlorides of metals acidified with hydrochloric acid heretofore have been considered to be unsuitable for the electro-analytical deposition of metals, probably on account of the oxidizing effect of the liberated chlorine. Since the liberation of chlorine can be prevented by the addition of a reducing agent, and since such electrolytes present all the advantages of *simple, acid electrolytes* desirable for electro-analytical work, while in many respects they are more serviceable or convenient than either the "nitric acid" or the "sulphuric acid" electrolytes advocated by Foerster[1] and by Sand[2], we decided to investigate their use, particularly with metals such as copper, antimony, bismuth, and tin for which hydrochloric acid electrolytes are generally considered to be unsuitable, and for two of which,—namely, antimony and tin—the use of any simple acid electrolyte cannot be said to have been made *practicable* even by the recent excellent work of Sand.[3]

We have found that copper, antimony, bismuth, and tin may be deposited quantitatively and in good form from "hydrochloric acid" electrolytes if suitable reducing agents (formalin, hydroxylamine hydrochloride, oxalic acid, etc.) are added to them. By these means, we have also found it possible to separate copper from tin and determine both from the same sample of electrolyte, thus reducing the otherwise troublesome analysis of bronze[4] to a very simple operation; and we have found that metals with a potential "more zincic"[1] than that of tin do not interfere with the determination of copper by this method.

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[1] *Foerster*, "Elektrochemie Waesseriger Loesungen," page 235. See also, Zeitsch. angew. Chem. 19 (1906) 1842.

[2] *Sand*, J. Chem. Soc. 91 (1907) 401.

[3] *Sand*, ibid, 93 (1908) 1573.

[4] Z. Elektrochem. 15 (1909) 591.

The essential fact that makes this electrolyte serviceable is the presence of the reducing agent. Very probably, the deposition of the metal takes place by the discharge of the "lower valence" ions, and the reducing agent serves, in effect, to change the "higher valence" ions to the "lower valence" ions.

These methods present many advantages over older methods. The electrolytes are easily prepared, because all of the metals are soluble in aqua regia, and all of their compounds are soluble either in this reagent or in hydrochloric acid. These electrolytes are free from odor as compared with the sulphide electrolytes frequently used for antimony and tin. The results indicate that the deposits obtained are probably free from inclusions; and the time required for the determinations characterizes these methods as "rapid" methods.

The experimental details and the results obtained are presented below under suitable headings. Further work along this line is in progress.

The Electrolytic Apparatus

All the work in this paper was done with the special form of Sand[2] electrodes designed by A. Fischer.[3] The only change made was in the manner of clamping the electrodes. This was modified so that either electrode could be removed without disturbing the other, and that after removal they could easily be replaced in the same position. This new arrangement also makes the assembled apparatus more rigid than before. For this purpose, two special clamps,[1] held by a glass rod, are placed on opposite sides of the stirrer to hold the electrode connecting rods which extend straight up from the concentric wire-gauze cylinders (the electrodes). The arrangement is shown in the accompanying figure. The rods are clamped in a V-shaped groove by a blunt-edged wedge, 3 cm. in length, and the wedge is fixed so that it moves straight in or out of the groove. Thus the platinum rods are gripped firmly, but without being injured.

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[1] The term "more zincic" is used here to denote a difference in electrode potential measured in the direction toward the zinc end of the *Series of Electrode Potentials.* The term "more noble" would be used to denote a difference measured in the opposite direction, i. e., toward the noble metal end of the Series.

[2] Sand, J. Chem. Soc. 91 (1907) 374.

[3] Fischer, "Elektro-Analytische Schnellmethoden" (F. Enke, Stuttgart) page 78, or Z. Elektrochem. 13 (1907) 469. The apparatus and electrodes we used were made by Fritz Koehler, Leipzig. They are shown in his catalogue, 6092 and No. 6100.

The stirrer was turned at a rate of 800–1000 revolutions per minute.

We have found this electrolytic apparatus extremely serviceable. The platinum electrodes are relatively light: the outer cylinder weighs about 15 grams, and the inner cylinder about 13 grams, which shows that they compare very favorably in price with any other form of electrodes used for this purpose.

The Determination of Tin

Preliminary experiments showed that, in the absence of a reducing agent, the greater part of tin present in a solution of stannous chloride acidified with hydrochloric acid can be deposited rapidly in good form, but that a remnant cannot be deposited even though the current is continued for a long period of time. However, when a suitable reducing agent is present, the metal is deposited *quantitatively*.

In all the determinations, the weighed quantities of "Baker's Analyzed" pure tin were dissolved, cold, in approximately 10c.c. of hydrochloric acid, sp. gr. 1.20. The tin dissolved in a few hours if placed in contact with platinum. The resulting solutions were diluted to approximately 200 cc., in which concentration they were subjected to electrolysis. The reducing agents were added in the form of pulverized solids or in the form of concentrated solutions, so that their addition did not affect the concentrations materially.

The *maximum current density* with which *a good deposit* of tin may be obtained out of the "hydrochloric acid" electrolyte

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[1] This special clamp, as designed by one of us, can be obtained from Fritz Koehler, (Catalogue No. 6205).

decreases as the concentration of the tin salt increases. With amounts of tin as high as 0.7 grams in 200 c.c., a current of 1.5 amperes gave us with our electrodes a good deposit at all temperatures at which we worked, i. e. 30° to 70°C. With higher current densities, such relatively concentrated solutions gave granular deposits, but with solutions of lesser concentrations, good deposits may be obtained with somewhat higher current densities. As 0.7 grams would be as large an amount of tin as would ever be used in an analysis, and as 1.5 amperes could hence be safely used in any case, we have used a current of 1.5 amperes in all our determinations.

The results obtained with different reducing agents will now be considered.

When hydroxylamine hydrochloride is present in the "Hydrochloric acid" electrolyte, tin is deposited quantitatively in a short period of time. The results obtained are given in Table I.

When formalin is present, the deposition of tin is incomplete, but more expensive than without a reducing agent. This is surprising because in some respects formalin is a stronger reducing agent than hydroxylamine. It may be due to the fact that formalin acts as an oxidizing agent towards energetic reducing agents.

When oxalic acid is present in the "hydrochloric acid" electrolyte, tin is deposited almost, but not quite, completely, as the figures in Table I show.

TABLE I

Tin Used	Reducing Agent	Time	Tin Deposited
.4370	4 grams NH_2OH, HCl	95 min.	.4380
.2460	do.	90 "	.2466
.6972	do.	90 "	.6970
.3046	do.	120 "	.3052
.3000	do.	120 "	.3000
.3580	10 grams Oxalic Acid	75 "	.3572
.3830	do.	75 "	.3822
.2070	do.	85 "	.2064

As is well known from Classen's ammonium oxalate method, tin may be completely deposited out of an electrolyte to which both ammonium oxalate and oxalic acid have been added. Classen's method thus appears as a special example of our general method. However, the oxalate methods heretofore employed have some undesirable features: the procedure recommended by Classen gives an excellent deposit, but requires a long period of time (nine hours); while Exner's rapid method requires the use of a "hot saturated" solution of ammonium oxalate, which is somewhat troublesome to handle, and the deposit obtained is loosely adherent and powdery. Hence an improvement of the oxalate method is desirable, and since we have found that the maximum current density with which a good deposit of tin may be obtained from this oxalate electrolyte *increases as the concentration* of the tin *decreases*, we concluded to combine this fact with the fact stated at the opening of this section on the "Determination of Tin". Thus we obtained the following method:

The greater part of the tin is deposited rapidly out of the simple "hydrochloric acid" electrolyte without a reducer, and then ammonium oxalate and oxalic acid are added and the remnant of tin is deposited *fairly rapidly*. By these means, an excellent deposit of tin is obtained in about 90 minutes, which places the method in the list of rapid methods. The results we have obtained with this method are presented below in Table II.

The table shows that the temperature range within which tin can be deposited by this method extends up to 70°C. At 75%, the tendency of the stannic salt to hydrolize becomes so great as to render this method impracticable.

In Table II, the column under "Time I" shows the number of minutes during which the "original hydrochloric acid" solution was electrolyzed, and "Time II" shows the number of minutes during which the solution was electrolyzed after the addition of ammonium oxalate and oxalic acid.

TABLE II

Tin used.	Temp.	Time I. minute.	Oxalate added.	Oxalic Ac. added.	Time II. minutes.	Total Time.	Tin Deposited.
.3112	50–60°	45	4 grams	10 grams	45	90	.3114
.3088	"	45	7 "	18 "	45	90	.3092
.3157	"	60	7 "	18 "	45	105	.3156
.3542	"	60	7 "	18 "	45	105	.3537
.4852	"	75	7 "	18 "	45	120	.4849
.6838	"	80	10 "	18 "	55	135	.6834
.3550	"	45	7 "	16 "	45	90	.3550
.2675	"	45	7 "	17 "	45	90	.2674
.2608	"	45	4 "	10 "	30	75	.2606
.3110	30–35°		Not weighed.	Not weighed.		120	.3114
.3862	"		"	"		120	.3862
.3482	"		"	"		120	.3479
.3816	"		"	"		120	.3809
.5964	"		"	"		150	.5958
.3862	60–70°		"	"		120	.3864
.4506	"		"	"		120	.4506
.4670	"		"	"		120	.4667
.6944	"		"	"		150	.6944

The Determination of Copper and Its Separation from Other Metals

It is impossible to deposit copper in good form from a simple solution of cupric chloride acidified with hydrochloric acid, but in the presence of hydroxylamine hydrochloride, formalin, or—less suitably—tartaric acid, copper can be deposited quantitatively. The "most zincic" cathode potential with which copper may be obtained in good form is approximately—0.60 volts against the "normal" calomel electrode[1]: this is approximately the potential with which hydrogen begins to be evolved from this electrolyte on the copper deposit, and the appearance of hydrogen may hence be used as an indication that the applied voltage is too great. The determinations marked "hydrogen limit" in Table III below have been made in this way, i. e. by keeping the current and voltage just low enough to avoid the

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[1] For a description of the method of measuring electrode potentials with this electrolytic apparatus, see Smith, *Electro-Analysis*, fourth edition, pages 274–282. The algebraic sign in front of the number of volts designates the polarity of the measured electrode in the *cell* formed between this electrode and the auxiliar (the normal calomel) electrode. In the above example, the gauze cathode is the negative pole of the cell composed of this electrode together with the *calomel* electrode.

TABLE III

Number of Exp.	Copper Used	Other Metals present	Reducing Agts. in grams.	Volts applied	Amperes	Cathode control	Time Min.	Copper deposited.
1...	.2700	none	10 cc. formalin	1.-1.6	3-.05	—0.40	45	.2698
2...	.3772	do.	do. 40% sol.	do.	do.	do.	50	.3770
3...	.3084	do.	do.	2.0-1.6	4-.05	do.	30	.3080
4...	.3962	do.	do.	do.	do.	do.	30	.3960
5...	.5194	do.	10 grams Tart. Ac.	2.0-1.5	7.0-0.0	do.	180	.5196
6...	.3292	do.	do.	2.3-1.3	8-0	do.	70	.3298
7...	.3785	do.	do.	2.1-1.5	7-0	do.	150	.3780
8...	.3642	do.	do.	do.	6-0	do.	70	.3650
9...	.4624	Ammonia.	do.	2.1-1.5	7-0.1	do.	130	.4616
10...	.3000	Ammonia.	do.	2.0-1.5	6-0.1	do.	160	.2995
11...	.4320	Sodium.	do.	2.2-1.5	7-0	do.	75	.4316
12...	.3411	Potassium.	do.	1.9-1.5	4-0	do.	140	.3412
13...	.5520	Potassium.	do.	1.8-1.5	3-0	do.	180	.5510
14...	.5650	Cadmium.	do.	2.3-1.5	6-0	do.	60	.5640
15...	.2535	Nickel.	do.	1.9-1.5	4-0	do.	85	.2528
16...	.5120	Cobalt.	do.	2.0-1.5	4-0	do.	60	.5118
17...	.5072	Chromium.	do	2.0-1.5	4-0.1	do.	180	.5070
18...	.5618	Chromium.	do.	2.1-1.5	6-0	do.	205	.5612
19...	.4222	Manganese	do.	2.0-1.5	4-0.3	do.	190	.4222
20...	.7342	none.	2 grams NH_2OH, HCl	2.1-1.2	6.5-0	do.	30	.7328
21...	.6136	do.	do.	2.8-1.4	7.5-0	do.	30	.6139
22...	.2922	do.	do.	2.0-1.2	4-0	do.	20	.2918
23...	.3552	do.	do.	2.0-1.2	4-0	do.	15	.3548
24...	.4016	do.	do.	2.0-1.2	5-0	do.	15	.4015
25...	.4624	Iron.	do.	1.6-1.3	4-0.5	do.	50	.4622
26...	.4232	None.	do.	2.5-1.0	10-0	—0.60	10	.4230
27...	.4094	do.	do.	2.4-1.65	8-0	do.	25	.4100
28...	.4006	do.	do.	2.2-1.65	7-0.1	do.	35	.4000
29...	.3426	do.	10 cc. formalin,	2.35-1.65	8-.2	do.	20	.3426
30...	.6320	do.	do. 40% sol.	2.5-2.0	10-0.1	do.	45	.6318
31...	.4378	do.	do.	1.8-1.4		Hydr. Limit.	45	.4374
32...	.2598	do.	do.	1.8-1.6	2-.05	do.	50	.2598
33...	.2880	do.	2 grams NH_2OH, HCl	1.6-1.2	2-.05	do.	60	.2882
34...	.4388	do.	do.	1.5-1.5		None.	25	.4392
35...	.4640	do.	do.	do.		do.	45	.4638
36...	.6436	do.	do.	do.		do.	50	.6434
37...	.3485	Tin.	do.	1.6-1.5	3-0	—0.40	30	.3486

evolution of hydrogen. Copper may also be completely deposited with a cathode potential as low as —0.40 against the "normal" calomel electrode—a fact that makes possible the separation of copper from tin. And finally, its deposition may also be controlled simply by limiting the total applied voltage, as was done in Experiments 34, 35 and 36 in Table III.

Kahlbaum's Electrolytic Copper was used for the determinations below. It was dissolved in aqua regia, and the solution evaporated to dryness or sufficiently extensively to expel the free chlorine and oxides of nitrogen, etc. An amount of hydrochloric acid which varied from 5 to 25 cc. (sp. gr. 1.20) and the reducing agents were then added, the solution was diluted to about 200 cc., and subjected to electrolysis.

As the results in Table III show, copper is readily separated from tin and from all metals "more zincic" than tin. For its separation from cadmium, nickel, cobalt, chromium, and manganese we found that tartaric acid could be used although this reducing agent appears to us to be the least suitable for the deposition of copper, and hence formalin or hydroxylamine would do as well; but for its separation from iron, tartaric acid was found to be unsuitable, and hence hydroxlyamine hydrochloride was used. For the separation of copper from tin, only hydroxylamine was used.

Special attention should be called here to the fact that the observing and limiting of the cathode potential for the quantitative deposition of a metal furnishes the operator a reliable, automatic indication of the "end point": as the amount of the metal in the solution approaches, and *finally becomes*, zero, the operator finds it necessary to reduce the applied voltage so that the current finally becomes zero (or retains a low, constant value). The "end points" of the determinations in Table III were ascertained in this way. This accounts for the differences in the length of time required for the different determinations; and it was on account of the greater length of time required for the deposition of copper in the presence of tartaric acid than in the presence of formalin or hydroxylamine hydrochloride that we considered tartaric acid to be the least suitable reducing agent.

The separation of copper from weighed quantities of tin and the subsequent determination of the latter was also tested, with the results given below. After removal of the copper by the method given above, the tin was determined by our "modified oxalate" method, because these determinations were made before we found that tin could be determined more readily by means of hydroxylamine.

Copper		Tin	
Used	Deposited	Used	Deposited
.5165	.5165	.6126	.6147
.4502	.4482	.3148	.3162
.3334	.3344	.2124	.2120
.5002	.5004	.5002	.5008
.5002	.5006	.5860	.5858

The analysis of an alloy of copper and tin (bronze) is thus reduced to the following simple procedure: Dissolve the alloy in aqua regia, evaporate the resulting solution to expel the free chlorine and oxides of nitrogen, add 2 grams of hydroxylamine hydrochloride and from 5 to 15cc. of hydrochloric acid, sp. gr. 1.20, and water sufficient to make the total volume about 200cc. Electrolyze with the Sand-Fischer electrodes, limiting the cathode potential to —0.40 volts against the "normal" calomel electrode. The copper will be completely deposited in from 20 to 40 minutes, and the "end point" will be recognized by the fact that the current will have to be reduced to zero to prevent the cathode potential from rising above the limiting value. Lower the beaker away from the electrode, and wash the latter with a jet of water, catching the wash water in the beaker containing the electrolyte. The amount of water required for this purpose will be only a few cc., which will not increase the volume of the electrolyte materially. The cathode is detached, dipped in alcohol and in ether, dried high above a flame, and weighed immediately. Since this electrode is copper plated, it may be used immediately for the deposition of the tin. Another portion of 3 grams of hydroxylamine hydrochloride is then added to the solution, and the solution is electrolyzed again with a constant current of 1.5 amperes. From 20 to 40 minutes will be required to deposit the tin. The end point may be ascertained by means of hydrogen sulphide.

The Determination of Antimony

In the determination of antimony from acidified chloride solutions, several peculiar properties of its salts must be considered. If hydrogen is evolved during the electro-deposition of the metal, some of the latter will be lost in the form of stibine. If the electro-deposition takes place at temperatures below 50°C, the impure "explosive" antimony is deposited.[1] At temperatures above 50°C, the tendency of the solutions to hydrolyze increases rapidly and is decidedly marked; and if the pentachloride is present, it will volatilize appreciably at these higher temperatures. The following procedure was designed to avoid errors arising from any of these causes.

Weighed samples of antimonious oxide, Sb_2O_3, "Baker's Analyzed," were treated with 20–25cc. of hydrochloric acid, sp. gr. 1.20, and with 2 grams of hydroxylamine hydrochloride. The resulting solution was diluted to 200cc., heated to a temperature between 50° and 75°C, and electrolyzed with the cathode potential limited to −0.40 volts against the "normal" calomel electrode. The following results were obtained.

Sb_2O_3 used	Antimony		Time Minutes
	In Sample	Deposited	
.6990	.5825	.5814	15
.4390	.3658	.3647	10
.5542	.4618	.4600	10
.2456	.2047	.2048	8
.4708	.3923	.3928	15
.4844	.4038	.4044	5

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[1] Z. phys. Chem. 52 (1905) 129.

The Determination of Bismuth

In order to obtain a good deposit of bismuth out of a "hydrochloric acid" electrolyte to which hydroxylamine hydrochloride has been added, it was found necessary to limit the cathode potential to —0.25 volts (against the "normal" calomel electrode until most of the metal had been deposited, and then, to deposit the last portions, the voltage had to be raised gradually until the cathode potential was —0.60 volts (against the "normal" calomel electrode) during the last few minutes before the current was interrupted.

"Baker's Analyzed" pure oxychloride of bismuth was used for the following determinations. The samples were dissolved in 5 cc. of hydrochloric acid, sp. gr. 1.20, 2 grams of hydroxylamine hydrochloride were added, the solution was diluted to 200cc., heated to a temperature between 55° and 75°C, and subjected to electrolysis in the manner stated above. The following results were obtained.

$BiOCl$ used	Bismuth		Time minutes
	In Sample	Deposited	
.3726	.3012	.3006	20
.5650	.4568	.4564	12
.3666	.2964	.2956	32
.3346	.2705	.2700	25
.4764	.3852	.3852	20

THE COPRECIPITATION OF COPPER AND CARBON BY ELECTROLYSIS: OXIDATION AT THE CATHODE

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Carbon has been found in the deposit obtained by electrolizing iron and nickel solutions [1] but we have not discovered any reference in the literature to the presence of carbon in electrolytic copper. In fact Lambris states definitely [2] that carbon is not precipitated at the cathode with copper under the same experimental conditions in which it is found in nickel deposits. We have succeeded in proving that carbon is precipitated at the cathode during the electrolysis of a copper sulfate solution containing a little nitric acid and a small amount of gelatin.

Experimental Conditions

Copper sulfate solution:

60 grams of pure blue vitriol were dissolved in water and made up to one liter.

Gelatin Solution:

One gram of gelatin was allowed to soak over night in water, gently warmed until solution was complete and made up to 100 cc. The gelatin should be of the best quality in order to obtain good results.

Solution for Electrolysis:

To 25 cc. of the solution of copper sulfate the desired amount of nitric acid and gelatin were added and the solution made up to 100 cc.

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[1] Lambris, Zeit. fur Elektrochemie, *15*, 973.

[2] l.c.

Electrodes:

The cathode was generally a rotating platinum crucible. Highly polished iron, brass or copper rods serve very well. Good results are more difficult to obtain with stationary electrodes. The anode was either platinum or copper. The latter was chosen when it was desirable to keep the concentration of the copper constant.

Duration of Electrolysis:

The electrolysis was often continued until all the copper had been precipitated. Generally, however, the process was interrupted after about ten minutes.

Further experimental conditions of a few of our electrolyses are given in the following table:

TABLE I

No.	C.C. Gelatin	N.C.D.	C.C. HNO_3 (1.2.)	Appearance and structure of deposit
1	0.0	3.6	1	Crystalline deposit, adhered well to cathode.
2	0.2	"	"	Good smooth deposit, dull in lustre.
3	1.0	"	"	Smooth, very shining deposit.
4	0.2	"	2.5	Good shining deposit.
5	0.5	"	"	Shining deposit, deep copper red.
6	1.0	"	"	Good shining reddish-black deposit.
7	2.0	"	"	Shining black deposit, peeled on drying.
8	4.0	"	"	Deposit fell off the cathode.
9	3.0	5.0	3.0	Beautiful shining dark red deposit.
10	3.0	10.0	"	Deposit peeled.
11	10.0	5.0	"	Dark dull deposit peeled.

Numbers 9 and 10 were carried out with a freshly prepared solution of very good gelatin.

From the above table it will be seen that if either the current density or the concentration of the gelatin becomes too high the deposit peels off the cathode during the electrolysis or afterward while the deposit is being dried. A great deal depends upon the gelatin. Some samples have no effect on the deposit until the electrolysis has been carried on for several minutes.[1] Other samples will not give a good deposit under any circumstances.

If the nitric acid is too dilute the gelatin has no effect on the character of the deposit. If the concentration is increased beyond that employed in the table the deposits are no longer black but copper colored if increased too much there is no deposit formed unless the current density is also increased.

In order to determine whether or not the deposit contained gelatin or some of its decomposition products about two grams of the black substance that had peeled off the cathode were heated in a current of oxygen freed from carbon dioxide by bubbling through a strong solution of potassium hydroxide. From the heated deposit the gas was led into a solution of barium hydroxide. A white precipitate was formed showing that the original deposit must have contained carbon either in a free or combined state. The carbon dioxide might come, of course, from the gelatin that had been precipitated with the copper.

Some of the black deposit was treated for a long time with strong ammonium hydroxide in the presence of air. A very fine black substance was left that on drying resembled lampblack. Furthermore, several smooth shining black deposits were dissolved separately in a solution of cupric and potassium chlorides. The resulting solution when filtered cold did not leave any black residue on the filter paper. If the solutions were boiled before filtering a black residue was left that could not be dissolved in hydrochloric or dilute nitric acid. The solution of the chlorides alone when boiled and filtered left no residue. This would indicate either, that the carbon was in a colloidal state when the deposit was first dissolved in the chlorides, or that the carbon was in a combined state and was set free by the boiling process.

In order to determine whether or not the anodic processes had any influence on the precipitation of carbon with the copper the cathode was enclosed in an unglazed porcelain cell. The deposits obtained even during the first minute or two did not differ in the slightest from those where the cathode was not enclosed.

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[1] Kern and Jarvis, Trans. Amer. Electrochemical Soc. *20*, 15.

THEORETICAL CONSIDERATIONS

There are several theories for the precipitation of carbon at the cathode. Foerster[1] regards the phenomenon as a physical one in which the carbon assumes the colloidal form and is thrown down with the metal. Verwer[2] believes that carbon dioxide on reduction gives the free carbon, while Lambris[3] has shown that either carbon dioxide, carbon monoxide or acetylene may cause the deposition of carbon at the cathode.

Our experiments do not enable us to definitely conclude whether the carbon goes into the deposit because of primary or secondary reactions at the electrode, nor whether it is there in a free or combined state. It seems probable, however, from the color of the deposit and from the fact that a black residue remains after treating the deposit with ammoni-hydroxide that at least a portion of the carbon is free.

We have not succeeded in proving that the black deposits do or do not contain cupric oxide. The dark color may also be due in some degree to the presence of finely divided copper.

Before carbon can be set free from gelatin an oxidation must take place, and therefore the assumption of an oxidizing action at the cathode seems justified. This point of view is further supported by the experimental fact that carbon can be thrown down with copper only in presence of oxidizing agents. Reducing agents will completely prevent its precipitation. It can be most easily obtained when nitrous or nitric acids are present in the solution for electrolysis. A concentrated solution of nitrates also gives the black shining deposit. The oxidation is doubtless due to secondary reactions at the electrode. The investigation is being continued by the use of an ultramicroscope.

[1] Zeit. fur angew. Chemie, *19*, 1847 (1906).

[1] Chemiker-Ztg. *25*, 792.

[3] l.c.

SUMMARY

In this article it has been shown experimentally that carbon can be precipitated with copper at the cathode.

Evidence is given to indicate that at least some of the carbon is in a free state in the deposit.

It is concluded from the experiments that an oxidizing action must have taken place at the cathode. This oxidation is probably due to secondary reactions.

THE FUNCTION OF INORGANIC ADDITION AGENTS IN THE ELECTROLYTIC DEPOSITION OF COPPER

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Many substances, such as sodium chloride, nitric acid, gelatin, tannin, etc. have a beneficial effect on the deposit if they are added under proper conditions during the electrolysis of copper solutions. A theory for the effect of colloidal substances has been proposed by E. Mueller[1] but a great deal of work must be done on the migration of organic colloids under the influence of the electric current before the theory can be satisfactorily vindicated.

Although attempts have been made[2] no adequate explanation for the effect of inorganic substances has been given up to the present time. The endeavor is made in this article to explain the function of these agents and the theory advanced is as follows. All addition agents that have a beneficial effect on the deposits either dissolve copper directly or serve to keep it in solution, either in colloidal or crystalloidal form.

The metal precipitated by the current has a tendency to redissolve, and the rate at which it goes into solution will depend to a large extent on the state of division. A very bad deposit consisting of loose finely divided metal, and perhaps some oxide, will dissolve faster than a smooth deposit because the former has a much larger surface exposed. It is an experimental fact that copper can be redissolved off the cathode during the passage of the current provided that the proper relations are maintained between the strength of the current and the solvent power of the liquid in the neighborhood of the cathode. We should, therefore, according to this theory obtain a good deposit when the conditions are such that copper in the form of extremely small particles, i.e. of molecular or colloidal dimensions, would be dissolved by the solution faster than it could be deposited by the current, and smooth copper would be deposited faster than it could be redissolved.

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[1] Zeit. fur Elektrochemie, *12*, 317.

[2] E. F. Kern, Trans. of the Amer. Electrochemical Soc. *15*, 441.
Ching Yu Wen and E. F. Kern, Amer. Electrochemical Soc. *20*, 121.

Substances, such as potassium chloride, do not dissolve copper directly; nevertheless they have an indirect bearing on the solvent tendencies of the liquid in that they form complexes with cuprous compounds and thus aid materially in keeping copper in solution so that it may be eventually thrown down on the cathode as a smooth deposit.

Although this idea was conceived before the writer saw the article by Mueller both these theories involve the same fundamental assumption, namely, that some particles of metal, because of some disturbing influences on the cathode, such as the evolution of a gas, become loosely deposited upon, or even completely detached from the cathode at the moment of giving up their electric charges. These particles may grow by the union of two or more to form a colloidal suspension. If the solvent power of the liquid in the vicinity of the cathode is such that the colloidal particles, which have a large surface exposed, are redissolved and therefore again assume the crystalloid form no bad deposit would be possible.

The theory[1] that the deposit is improved because of the reducing effect of the addition agents is untenable for it has been found[2] that sodium nitrate or sodium chlorate in the presence of free acid give good results. Even highly polished deposits of copper may be obtained from a solution of nitric acid containing a very small amount of gelatin.[3]

According to the theory of Mueller the beneficial effects of addition agents such as tannin or gelatin are due to the fact that these substances are protective colloids and prevent the colloidal copper particles which may be formed at the time of the discharge of the copper ion molecules, from falling out of solution. If the resulting combination of the copper particle and protective colloid has a positive charge the copper would eventually find its way to

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[1] Kern, Wen and Kern l.c.

[2] Wen and Kern, l.c.

[3] Spear, Chow and Chesley, these Proceedings.

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the cathode and be precipitated. The protective colloid would therefore be found in the deposit of copper on the cathode. This has been verified in many cases.[1]

The results of Kern could be explained by the theory of Mueller on the ground that the organic substances found to have a beneficial effect are either completely or partially colloidal, serve as protective colloids for the copper particles and move in the solution toward the cathode.[2]

The inorganic substances having the most marked effect on the character of the deposit in the electrolysis of copper are nitric, hydrochloric and sulfuric acids, nitrates, chlorides of ammonia and the alkalie and alkaline earth metals. Sulfates of these same cations are less efficient. The sulfates and chlorides dissolve copper in the presence of the cupric ion forming, in some cases, a complex where the copper is in the anion. A familiar example of this is in the determination of carbon in steel. The steel is dissolved in a solution of cupric and alkalie chlorides. Copper is at first precipitated on the iron but dissolves later as soon as all the iron has disappeared.

That copper redissolves in copper sulfate while the current is still going through the solution has been pointed out by Meyer in his work on the copper voltameter.[3] While equilibrium conditions could scarcely obtain during electrolysis with high current densities there is always the tendency toward the following reaction:

$$\mathrm{Cu}+\mathrm{Cu}\dagger\dagger \rightleftarrows 2\mathrm{Cu}\dagger$$

It may be that this is a factor in the formation of a bad deposit. After the concentration of the cupric ion becomes low small colloidal particles of copper would not be so readily redissolved and would therefore accumulate on the cathode to form a loosely adhering deposit toward the end of the reaction.

Nitric acid is the best solvent for copper in the above list and it is a significant fact in support of the theory that it is also the best inorganic addition agent for improving the character of the deposit. Nitrates are also efficient and that they have an oxidizing action is shown in the article by Spear, Chow and Chesley[1] on "The Electro-coprecipitation of Copper and Carbon."

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[1] Mueller, l.c.

[2] Northrup and Hering, Trans. Amer. Electrochemical Soc. *10*, 35.

[3] Meyer, Zeit. fur Elektrochemie, *15*, 12; also, *15*, 65.

Copper cannot be thrown out of solution if the concentration of the nitric acid is too great obviously because the acid dissolves the deposit faster than the current can form it. We should say perhaps that the electrode potential is such that something else beside copper is liberated at the cathode. As the electrolysis proceeds the nitric acid is slowly removed by the current and the copper can be completely precipitated if the process is continued long enough.

From these considerations it should be possible to correct a bad deposit of copper by adding a little nitric acid and electrolizing the solution for a longer time. At first the loose copper should be dissolved off the electrode and again be precipitated as smooth copper. This proved to be experimentally possible. A loose dark fine grained deposit of copper was obtained by electrolizing a solution of copper sulfate with a rotating cathode. The electrodes were removed, washed, again put in place and sufficient current turned on to give a normal current density of three amperes. A solution consisting of 2.5 cc. nitric acid (1.42) in 100 cc. water was then raised to cover the electrodes. The solution turned blue in a few seconds showing that copper had been dissolved. After electrolizing for some time the solution again became colorless indicating that the copper had been reprecipitated. This experiment was repeated many times with varying concentrations of nitric acid. If the concentration of the acid were too great all the copper was dissolved off the cathode and none was redeposited; if it were too small there was no perceptible effect. The deposit was improved in every case where the acid was kept within the limits, 1.5–5cc. (1.42) per 100 cc. solution. As nitric acid is destroyed very slowly by the current under the above conditions these experiments show conclusively that the solution of loose copper and its redeposition in a smooth form can go on simultaneously on the cathode which is a fundamental assumption of the theory.

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[1] Spear, Chow and Chesley, l.c.

It is a familiar experience in electroanalysis to have a copper deposit become loose and worthless if the current is allowed to go through the solution too long, although the deposit may have been firm and adherent when the solution first became colorless. The theory explains this phenomenon on the ground that copper is being continuously dissolved and reprecipitated. It is dissolved off the entire electrode but is reprecipitated where the current is greatest, viz. on points on the cathode nearest the anode. If an electrolysis with stationary electrodes is left long enough copper will entirely disappear from the back of the cathode and be precipitated in the form of trees on the side nearest the anode.

The correction of a bad deposit by addition agents other than nitric acid is attended with results of a less positive nature as the theory demands because they are not so good oxidizing agents and therefore do not dissolve the copper so readily. Nevertheless an 8% solution of ammonium or sodium nitrate turned blue when brought in contact with a bad deposit although a normal current density of three amperes was maintained. Much more dilute solutions of nitrates will dissolve finely divided copper. It has not been ascertained whether the presence of air is essential or not.

SUMMARY

In this article the theory is advanced that the function of inorganic addition agents in the electrolysis of copper solutions is to keep the copper in solution.

The fundamental assumptions are:—

That some particles of copper may assume the colloidal form at the moment of giving up their electric charges at the cathode.

That oxidation may take place on the cathode during the passage of the current.

Experimental proof is given to show that copper is continuously dissolved and reprecipitated at the cathode during the electrolysis of copper solutions.

The theory explains the fact that good deposits of copper become bad if the electrolysis is continued too long.

GEGENWÄRTIGER STAND DER ENTWICKLUNG GROSSER ELEKTRISCHER OEFEN

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Wien, XIX.

Die Entwicklung der grossen elektrischen Oefen hat in den letzten drei Jahren wieder bedeutende Fortschritte aufzuweisen. Zunächst ist hervor zu heben, dass sich die Schliessung der grossen Oefen in der Praxis gut bewährt hat. Ein solcher Ofen ist in Deutschland nunmeh in swei jährigen Betrieb, und arbeitet vollkommen befriedigend. Seit einigen Monaten ist in Frankreich ein 10.000 HP Ofen in Verwednung und auch dessen Betrieb geht befriedigend von statten, und seine Arbeitsweise entspricht den Erwartungen. Weitere Anlagen sind in Deutschland und Schweden im Bau und kommen noch dieses Jahr in Betrieb. Wir wollen nun eingehend an Hand der Deutschen Reichspatente die Neuerungen der Oefen besprechen.

Das D.R.P. No 224878 schützt einen elektrischen Ofen, bestehend aus mehreren Ofenschächten (selbstständigen Arbeitsherden) deren Bodenelektroden leitend miteinander verbunden sind. Es unterliegt bekanntlich keiner Schwierigkeit kleine elektrische Oefen zu decken. Dagegen stiess man bei der Deckung grosser Oefen stets auf die Schwierigkeit die Decke mit ihrer grossen Spannweite gegen die im Ofen herschende hohe Temperatur, und dem dadurch verursachten Einbrechen der Decke zu begegnen, welches nach verhältnissmässig kurzer Betriebsdauer erfolgte. Diese starke Abnutzung ist eine Folge der grossen Spannweite. Die Erfindung des D.R.P.224878 löst die Schwierigkeit durch die Verminderung der Spannweite, ohne dass dabei die Einfachheit der Stromführung im Ofen leidet, dadurch dass der elektrische Ofen aus mehreren Ofenschächten besthet, deren Bodenelektroden leitend miteinander verbunden sind, und die leitende Verbidnung durch ein allen Schächten gemeinsames, stromleitendes Bodenmassiv (D) hergestellt ist, zum Zwecke, untere Stromanklemmungen und die hiermit verbundenen Gefahren und Nachteile zu vermeiden.

Die aus den Figuren 1 und 2 ersichtliche Ausführungsform der Herde im Dreieck hat sich in der Praxis gut bewährt namentlich dort, wo es sich um die Darstellung verschiedener Produkte, in den einzelnen Herden handelt. Die Erfindung nach dem D.R.P. 224878 ermöglicht es nämlich, in ein und demselben Ofenmassiv verschiedene Produkte gleichzeitig nebeneinander zu erzeugen, und erlaubt grosse Varationen der erzeugten Mengen der verschiedenen Produkte je nach der Marktlage.

Das D.R.P. 226956 beschreibt eine Beschickungsvorrichtung an elektrischen Oefen durch Aufsetzen einer Glocke wobei das Beschikkungsmaterial den Abschluss bilden kann. Nach vorliegender Erfindung werden diese Schwierigkeiten dadurch überwunden, dass über dem eigentlichen elektrischen Schmelzherd ein glockenförmiges, vorteilhaft an der Mündung verengtes Mischungsreservoir angeordnet ist, in welches die Materialzuführungsrohre münden und die ganzen Elektroden beweglich hinein hängen. Auf diese Weise wird nicht nur die Anbringung eines gasdichten Abschlusses in den Elektrodeneinführungsschlitz ermöglicht, es wird vielmehr auch eine wirksame Abdichtung durch die hohe Materialsäule erzielt.

In der beiliegenden Zeichnung ist der Erfindungsgegenstand veranschaulicht und zwar zeigt: Figur 3 denselben zur Hälfte im lotrechten längsschnitt, zum Teil in Ansicht.

Auf dem Rahmen I der äusseren Ofenhülle bzw. der Decke 2 ist eine Glocke 3 vorteilhaft durch übergreifende Leisten gasdicht aufgesetzt. Sie hängt mittels Ketten der Traversen unterstützt, in den Ofen hinein und ist an ihrem unteren Teil vorteilhaft wassergekühlt, so dass sie jeder Hitzebeanspruchung gewachsen ist. Sie ist in ihrer Ausdehnung derart bemessen, dass sie die Arbeitselektroden samt Fassung und rings um diese eine ausgiebige Materialmenge aufnehmen kann, wobei sie vom eigentlichen Schmelzherd derart entfernt ist, dass auch eine frische Elektrode vom Beginn ihres Einsetzens in den Ofen vollständig im Glockeninnern Platz hat, ohne Stromschluss in dem Inhalt des elektrischen Reaktionsherdes zu bekommen. Dadurch wird bewirkt, dass für die Elektrodenregulierung nur ein schmaler

Schlitz 5 am oberen Ende der Glocke für die Stromzuführungsschienen 6 und Elektrodenfassung nötig ist. Als gasdichten Abschluss besitzt die Glocke am oberen Rande um den Elektrodeneinführungsschlitz 5 den mit einem Wulstleisten 7 abschliessenden Hals 8. Ein gleicher Wulst 9 ist an der Stromzuführungsschiene 6 angeordnet. Ueber die Wulste wird gasdicht ein wassergekühlter Kautschukmantel gelegt, der vorteilhaft mit Asbesttuch oder Leder überzogen ist. Durch diese Anordnung ist eine beliebige Bewegung der Elektrode im Ofen unter vollständiger Dichtung des Schlitzes 5 ermöglicht, da die Bewegung der Elektrode bloss den Mantel zusammendrückt, welcher an seinen Fixpunkten 7 und 9 mit Leichtigkeit gasdicht anzubringen ist.

Das D.R.P. 235061 Fig 4 u. 5 schützt ein wichtiges Konstruktionsdetail nämlich die Auflagerung der Ofendecke und des Beschickungsbehälters in Form von wassergekühlten eisernen Trägern, welche sich auf die Ofenwand stützen. Dadurch wird die durch das D.R.P. 224878 bereits unterteilte Spannweite noch weiter vermindert, und gerade der gefährliche Raum um die Elektroden nur durch Mischung abgedeckt.

Das D.R.P. 229302 betrifft eine Erfindung welche die Betriebskontrolle der geschlossenen Oefen wesentlich erleichtert, dadurch, dass absperrbare Oeffnungen S in Fig 4 auf der Decke des Ofens seitlich des engeren Beschickungsschachtes angeordnet sind, zu dem Zwecke, den Ofenprozess und die Einführung der Mischung auch während einer kontinuirlichen Beschikkung beobachten und beeinflussen zu können. Die Anordnung ist aus der Figurleicht ersichtlich. Diese Schlitze haben noch den grossen Vorteil, dass sie es gestatten, die Mischung zu beeinflussen, denn es können durch diese Schlitze nicht nur Schüreisen zum Herabstossen der Mischung eingeführt werden, sondern auch Zusätze eingeworfen werden. Also Mischungskorrekturen sind von hier aus unmittelbar in Schmelzherd selbst vorzunehmen ohne dass die continuirliche Chargierung darunter leidet.

Das D.R.P. 239078 Fig 6 liegt die Idee zu Grunde, dass sich die elektrische Raffination die Vorteile der grossen elektrischen Oefen zu Nutze machen soll, und sie ist eigentlich eine Verbesserung der Oefen wie sie von Grönwal, Lindblad und Stahlhane für Erze vorgeschlagen worden sind, als Kombination von Hochöfen mit elektrischen Schmelzherden. Dadurch das hier doch eine römliche Trennung vom Hochofen vorgenommen ist, und vertikal hängende Elektroden verwendet werden, ist nicht nur die Regulierbarkeit der Elektroden eine erhöhte, sondern es werden auch Elektrodenbrüche vermieden, welche durch hängen bleiben der Mischung des Hochofens verursacht werden können.

Die Erfahrungen welche bei der Carbid und Ferrosiliciumerzeugung gemacht worden sind, müssen für die Eisenraffination besonders grosse Vorteile gewähren. Diese Vorteile sind in erster Linie die Selbstraffination infolge des hydraulischen Druckes in dem Reservoir von geschmolzenen Eisen. Diese Höhe beträgt ungefähr 100cm. Es ist leicht begreiflich, dass dadurch auch die letzten Spuren von Schlacke aus dem unten geschmol zenen Eisen an die Oberfläche gedrückt werden. Bei dem kleinen Raffiniröfen ist die Höhe des geschmolzenen Eisens kaum höher als 30cm., dort ist eine derartige quantitative Separation von geschmolzenen Eisen und Schlacke nicht so leicht möglich, ausserdem liegt dort wegen der geringen Höhe von geschmolzenen Eisen die Gefahr nahe, dass beim Abstechen des Eisens die auf der Oberfläche schwimmende Schlacke wieder in das bereits raffinierte Eisen eingesogen wird, eine Gefahr deren Wahrscheinlichkeit bei Abstechen der grossen Oefen, deren Abstiche sich auf mehrere Tonns belaufen, weitaus verringert ist. Die vorleigende Kombination des Hochofens mit dem elektrischen Ofen, findet bei den Eisenfachleuten noch Widerstand. Es handelt sich aber um einen Vorschlag, von grosser Tragweite, dem sich die Eisenindustrie nicht lange hemmend in den Weg stellen kann, umsoweniger da auch ein Weg gewiesen scheint, wie das schwierige Problem in einfacher Weise gelöst werden kann. Da der Hochofen nicht gerne zu Versuchszwecke herangezogen wird, einerseits wegen seinen hohen Kosten, anderseits wegen vielfachen Gefahren welche sein Betrieb mit sich bring will man dem ohnehin komplizierten Betrieb nicht durch Anhängen eines elektrischen Ofens weiter komplizieren.

Ganz anders aber liegen die Verhältnisse beim Kupoloofen, und für diesen Zweck dürfte die Kombination wie sie auch in der Patentschriangesprochen ist rascher und leichter Eingang finden.

So vor allem die Gewinnung schwer schmelzbarer Metalle, wie Kupfer und Nickel, dann aber auch für Giessereizwecke, wo die elektrischen Schmelzherde nicht nur ein grosses Reservoir für Giessereieisen bilden, sondern auch Guss von sehr hoher Temperatur liefern können, und den damit verbundenen grossen Vorteilen. Es findet aber auch durch den hydraulischen Druck bedingt, Selbstraffination statt, wodurch ein Qualitätsguss wird.

Die beiliegenden Photografien [1] zeigen neue Ofenanlagen, und geben eine Vorstellung von den Grössenverhältnissen der beschriebenen Oefen. Es wäre jetzt noch zu erwähnen, dass die Ermässigung der Erzeugungskosten schon durch die Einführung der grossen elektrischen Oefen eine bedeutende war. Während der Preis des verpackten Carbids ca. 18–20Kr bei den kleinen Oefen war, ist bei den grossen offenen Oefen auf ca. 15–16 Kr. reduziert worden. Durch das Schliessen der Oefen wurde der Preis wiederum veringert bis auf Kr. 12–13 unter den gleichen Verhältnissen.

Ferrosilicium konnte mit den kleinen Oefen überhaupt nicht ökonomisch gemacht werden, der Preis der Erzeugung von 50% Ferrosilicium veringert sich durch das Schliessen der grossen Oefen um etwa Kr. 20 per Tonne.—

Es ist eine unumstössliche Tatsache, dass die grossen geschlossenen Oefen am wirtschaftlichsten arbeiten, infolge ihres einfachen Betriebes, Ersparnissen an Elektrodenmaterial und Arbeitslöhnen, der geringeren Investition die durch die Grösse des Ofens an und für sich bedingt ist, dass heisst, Konzentration auf einen bedeutend kleineren Raum, dann aber auch besonders wegen der geringen Abnutzung des Ofens. Solche Oefen arbeiten bereits jahrelang ohne Reserve, denn nur die Elektroden und Decke unterliegen einer Abnutzung. Die Auswechslung der Elektroden ist aber eine sehr einfache, und Reparaturen an der Ofendecke bewirken keine Betriebsstörungen, sondern können ebenfalls im Betriebe durchgeführt werden. Unter diesen Umständen darf man sagen, dass die hier beschriebenen Oefen billiger arbeiten müssenals irgend ein anderer derzeit exestierender. Wenn aber dennoch gelegentlich Berechnungen mit niedrigen Erzeugungskosten von Carbid und Ferrosilicium gezeigt werden, so kann es sich entweder nur um einen Irrtum handeln,—oder um incommensurable Verhältnisse, wie z.B.beim Carbid nachstehender Fall vorkommen kann. Bekanntlich kann man die Ausbeute an Carbid bedeutend vergrössern, wenn man minderwertiges Carbid erzeugt, das einen Ueberschuss an Kalk enthält. Ein derartiges Carbid genügt aber vollständig den Ansprüchen der Cyanamidfabrikation, nicht aber den Formes des Marktcarbides für Acetylen.

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[1] Photographien zeigen je 2 Ansichten eines 6000 H P—und 12000 H P Bezeichnung auf der Rückseite der Photographien.

Das wichtigste Anwendungsgebiet, dass die grossen Ofen im letzten Jahr erobert haben, ist das Erschmelzen von Eisen aus seinen Erzen. Da es hier vor allem auf die Erzeugung grosser Massen ankommt, konnten die kleinen Ofenagregate wie zum Beispiel die von Grönwal nicht mehr genügen, desshalb hat die Stora Kopparbergs Aktiebolag, Falun einen Grönwalofen, denn Sie im jahrelangen Betrieb ausgearbeitet hatte stillgelegt, und errichtet gegenwärtig einen Helfenstein Ofen, der noch im laufenden Jahr in Betrieb kommen soll. Der Grönwal Ofen hatte sich zwar im kleinen Betrieb gut bewährt, als man aber im Domnarfvet nach der ersten Vergrösserung des Grönwalofens die Vorteile der grossen Ofen erkannt hatte, war man schrittweise zu 2.000 und 4.000 HP übergegangen. Die Vergrösserung war aber keine eigentliche Vergrösserung der Herde, sondern nur eine Vermehrung der Herde. Der Ofen der bei 2.000 HP 3 Schmelherde besitzt, besass bei 4.000 HP 6 Schmelzherde. Man projektierte sogar einen Ofen mit 9 Herden, der aber nicht zur Ausführung kam, denn es zeigte sich schon, dass das System schon bei 4.000 HP in Folge seiner Unzugänglichkeiten. Diese sind:

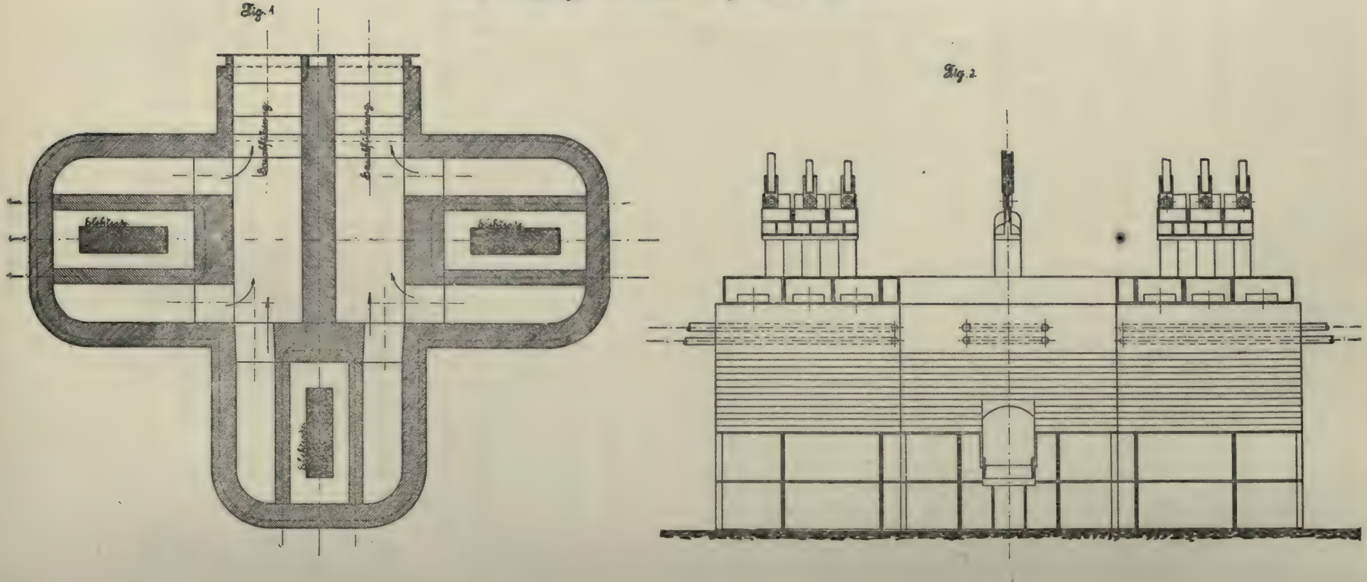
(1). Schräggestellung der Elektroden, welche bei hoher Belastung nicht mehr regulierbar und daher in ihrem Dimensionen begrenzt sind.

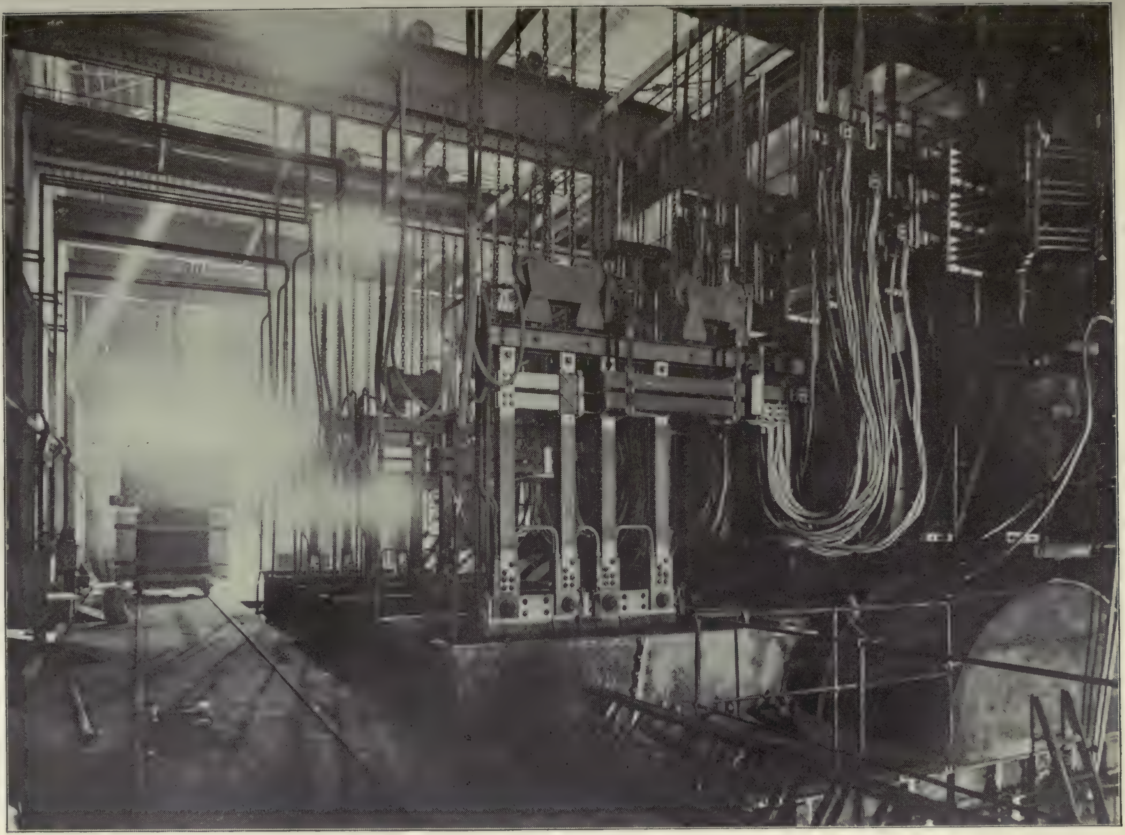
(2). In der Schachtform, welche durch Festhalten an der alten Hochofenform die Gefahren des Hochofens auch auf den neuen Ofen übertragen. Das Anlassen und Stillegen des Ofens war eine langwierige Operation welche mehrere Tage erforderte, dann war das Hängenbleiben eine grosse Gefahr weil durch das Nachrutschen Elektrodenbrüche verursacht wurden. Während im Dreiherdigen Grönwalofen wie oben bereits erwähnt nur 2.000 HP verwertet werden können, können in einem dreiherdigen Helfensteinofen 10.000–12.000 HP in einem 6 herdigen 24.000 arbeiten was einer Tagesproduktion von 250 Tonns Roheisen HP gleich kommt, somit eine Massenproduktion darstellt, wie sie die modennen Hochöfen erreichen.

Die Elektrifizierung der Eisenindustrie hat in Schweden und Norwegen die grössten Erfolge erzielt. In Trollhatten Domnarfvet Hagfors Hardanger und Arendal sind im Ganzen 25.000 HP für diese Zwecke verwendet. Die Kalkulation stellt sich in den beiden Ländern besonders günstig den 1 HP–Jahr ersetzt 2 Tonnen Brennstoff. Wenn also auf Qualitätseisen gearbeitet wird muss Holzkohle verwendet werden bei einem Preis von ca. 40 Mk. per Tonne somit einen Aezuivalent von 80 Mk per 1 HP–Jahr. Dem gegenüber stellt sich aber bekanntlich der Kraftpreis viel niedriger. Im Durchschnitt kann man annehmen, dass das HP–Jahr in Schweden mit 40 Mk. in Norwegen mit 25 Mk leicht zu beschaffen ist. Ist somit der elektrische Ofen in Skandinavien mit Bezug auf die Energiekosten dem alten Hochofen überlegen, so ist er dies auch in Bezug auf die Verwendungsmöglichkeit der Qualität der verwendeten Erze. Schon im Grönwalofen kann man 20% Schlich (pulvriges Erz) zusetzen, im Helfensteinofen dürfte man bis zu 80% gehen können. Dies ist besonders für Norwegen wichtig da dort die meisten Erze vorkommen schlichartig sind, d.h. zum Zerfallen beziehungsweise zum Zerbröckeln neigen. In Schweden hat die Regierung und namentlich auch der Stahlwerksverband (Jernkontoret) die Bedeutung der Elektrifizierung der Eisenindustrie für ihr Land schon vor vielen Jahren erkannt, deren Entwicklung ausgibig unterstüzt und schliesslich finanziert, so dass besonders dem Letzteren das Hauptverdienst an Aufschwung dieser hervorragenden neuen Industrie zukommt.

Dreiphasenofen

mit im Dreieck angeordneten Herden [System Dr A. Helfenstein]

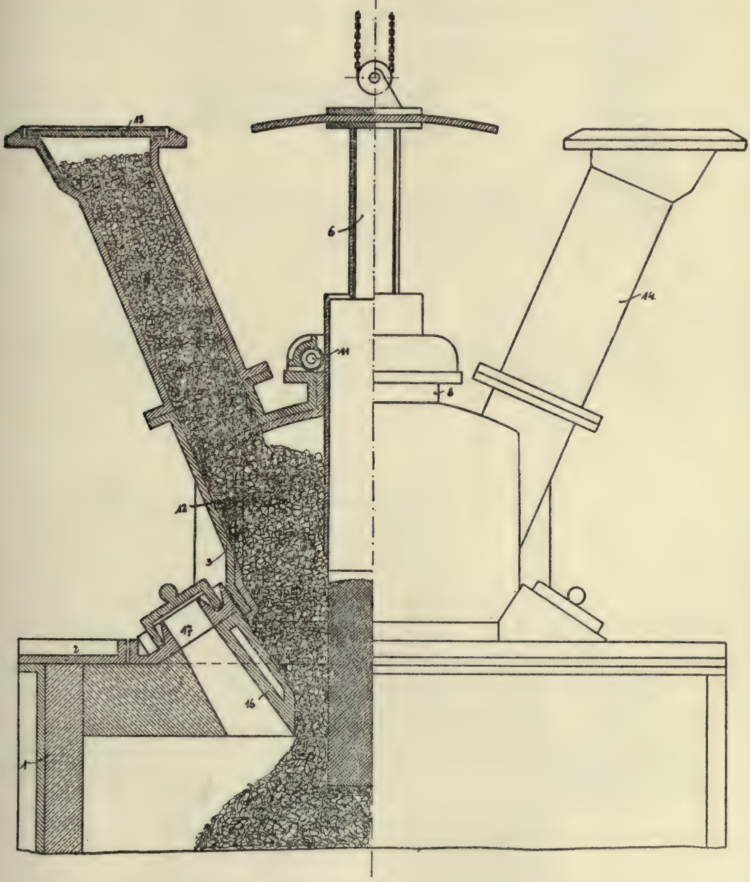




Helfenstein-Ofen für 12,000 H. P. für Ferrosilicium

Beschickungsvorrichtung für elektrische Öfen. [System Helfenstein].

Fig. 3.



Deckenanordnung für elektrische Öfen. [System Dr O. Helfenstein.]

Fig. 4.

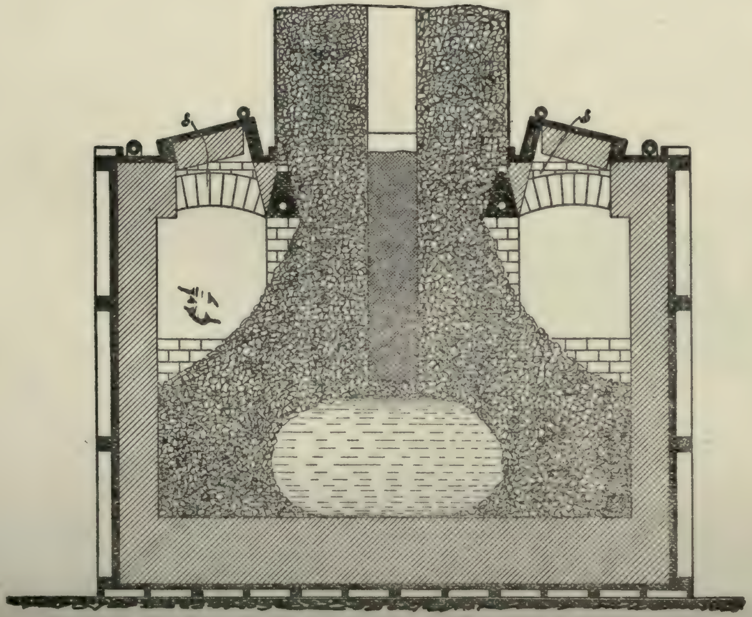
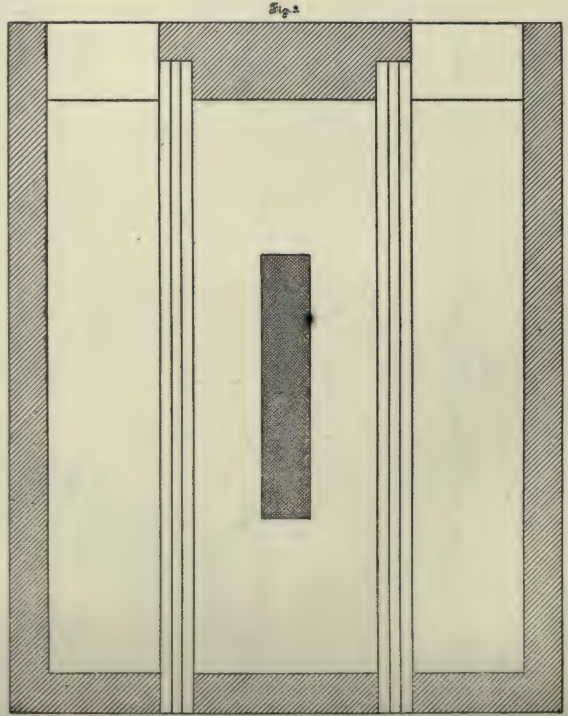


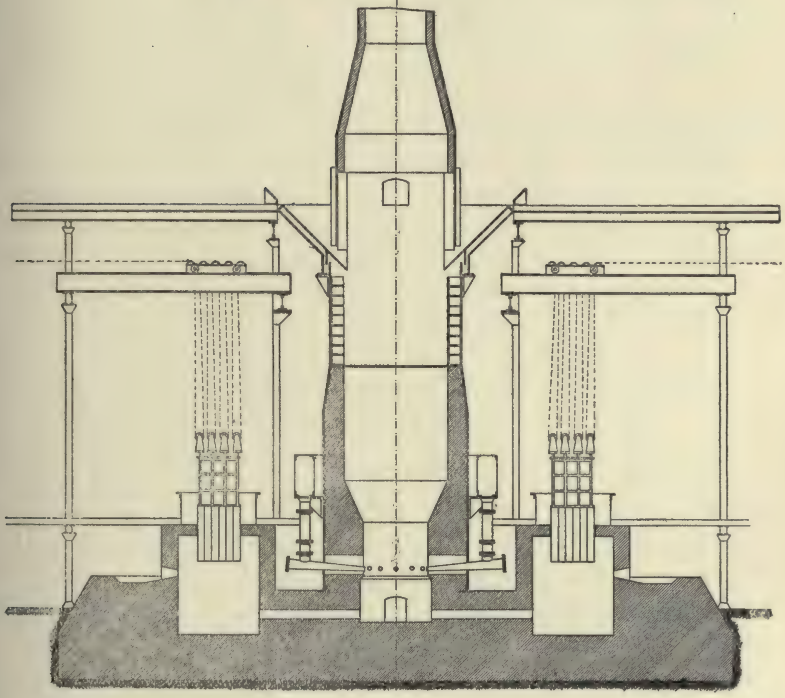
Fig. 3



Kupolofen

mit elektrischer Raffiniereinrichtung. (System Dr A. Helfenstein).

Fig. 6



A DEVICE FOR CONTROLLING SMALL ELECTRIC FURNACES

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The plan described herewith for maintaining any desired temperature in a small electric furnace was devised for use with a 10 kilowatt carbon plate resistance furnace, for which direct current only was available.

It is usual to employ alternating current for such furnaces, reducing the voltage as the resistance of the furnace falls with the rising temperature.

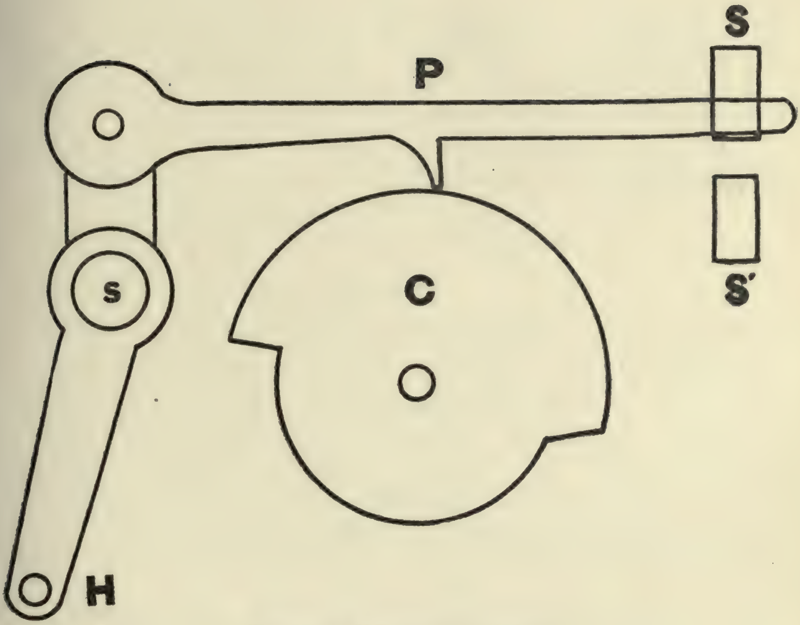
Where direct current is used, the control is usually effected by means of a rheostat, which, of course, wastes a considerable portion of the energy. The present plan dispenses with the use of a rheostat, by automatically opening the circuit once a minute and closing it after an interval regulated at will.

The control is effected by means of a small motor, which drives, by small gears, a cylindrical cam (C) 250 mm. (9.87″) long and 50 mm. (1.97″) in diameter, the cylinder being cut away on a taper from 350° at one end to 0° at the other. The pawl (P) is carried on a screw (s), which can be turned by the handle (H) to set the pawl quickly and accurately to any desired position. When the pawl is resting upon the cam, the control switch (S) is closed. This automatically closes the clapper switch carrying the current; when the pawl drops, the control switch (S′) is closed, opening the clapper switch and cutting off the supply of energy from the furnace.

It is evident that the fractional amount of time during which the current is supplied to the furnace varies with the position of the pawl on the cam. While heating the furnace, the automatic switch is at rest; when the desired temperature has been attained, the motor which actuates the switch is started and the cam set to the position which has been found by trial to furnish the energy required to balance the losses by radiation. The pawl may be set with ease to within 1 mm. (.03937″), which is, of course, a finer adjustment than is required.

The control of the furnace is further effected by placing in series with the carbon resistance an auxiliary resistance of .2 ohm of nichrome tape, which increases to .3 ohm at the maximum temperature. The furnace is operated at 1300° Cent (2372° Fahr.), and since this is too high for the nichrome to withstand permanently, the latter is placed in the base of the furnace, where the temperature does not exceed 1100° Cent. (2012° Fahr.). The increase of resistance of the nichrome with the rise of temperature tends to offset, in some measure, the diminishing resistance of the carbons, and so to prevent any accidental overheating of the furnace in case of failure of the operator to look after the adjustment of the controlling device.

The chief advantage of this plan over the rheostat is in the saving of energy. All the energy consumed is delivered to the furnace, except the small amount (about 50 watts) required to run the motor, and the much smaller quantity required to actuate the switch.



ELECTRIC FURNACE CONTROL

THE ACTION OF NITROGEN ON STRONTIUM CARBIDE

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The action of nitrogen on lithium carbide has already been investigated[1] and the present work with Strontium Carbide was taken up in the same manner, and included the following:

(1) Preparation of strontium carbide and analysis of the product.

(2) Absorption of nitrogen by the carbide and the influence of time, temperature, and pressure.

(3) Analysis of the product and conclusions.

Preparation of Strontium Carbide

Moissan[2] obtained strontium carbide under the same conditions as the carbide of calcium, by heating a mixture of 150 parts strontium carbonate and 50 parts of sugar carbon in his horizontal arc furnace. The power used is stated at 24.5 K.W., using 350 amperes at 70 volts. The duration of the run was 15 minutes. The product obtained by Moissan was a blackish mass with a crystalline brown fracture and is decomposed in moist air, and agrees in its general properties with the other alkaline earth carbides.

In the preparation of strontium carbide for this work, the same general method was employed. The furnace used was the vertical arc type[3] consisting of a graphite crucible about 4″ diameter which constitutes one of the electrodes, the other electrode is a vertical graphite rod. Proper heat insulation is provided and the heating can be carried on by direct arc or partially by resistance. Strontium Carbonate and coke were used for the raw materials and both were selected with a view to their purity. On heating to a temperature of about 2000° C the following reaction takes place:

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[1] Tucker and Moody, Jour. Am. Chem. Soc. XXXIII 1911, 1478.

[2] Le Four Electrique 301, Paris 1897.

[3] Tucker Vertical Arc Furnace Electrochem. & Met. Eng. IV. 263.

$$SrCo_3+4C=SrC_2+3Co.$$

A number of runs were made to ascertain the best conditions of heating and the proportions of the charge best suited to the formation of the carbide which might differ from the theoretical. The difficulties arising in the preparation of strontium carbide are the same as are found in the formation of lithium carbide[1] from the fact that its formation and decomposition temperatures lie close together resulting in the presence of decomposition products in the resulting carbide. The tendency however is less prominent with strontium than it is with lithium and for that reason it is much easier to prepare the carbide of strontium. The value of the carbide was determined by evolving the acetylene from a weighed sample in a Rose and Geissler Alkalimeter by the application of cold water, as follows:

$$SrC_2+2H_2O=C_2H_2+Sr(oH)_2$$

The gas was carefully dried by passing over calcium chloride, the loss in weight being equivalent to the acetylene evolved. About 150 grams of the mixture of the carbonate and coke were taken for each run the data of which is given in the following:

TABLE I

No.	Time minutes	Power	Product Carbide Content
1	5	2.5 K.W.	72%
2	6	3.2 "	73%
3	12	3.0 "	72%
4	15	3.0 "	73%
5	22	3-4.2 "	62%
6	25	3-4.2 "	60%

Alternating current was used with about 35 volts at the arc. Nos. 5 and 6 were samples from the product of #3 and #4, heated for 10 minutes further at a slightly increased power and shows that prolonged heating results in decomposition and consequently a lower value of the carbide content.

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[1] Tucker-Moody Jour. Am. Chem. Soc. XXXIII 9, 1480.

Absorption of Nitrogen by the Carbide

The nitrogen for this part of the work was prepared chemically, by heating a strong solution of ammonium chloride in a large flask and introducing a solution of sodium nitrite gradually by means of a stop cock funnel tube. By regulating the supply of the nitrite in this way a brisk evolution of the gas can be maintained. After washing the gas was stored in gasometers until required for use. The gas so prepared contains a small quantity of oxygen, and in order to remove this, it is necessary to pass the gas over copper gauze heated to a low red heat in a combustion furnace.

The nitrogen obtained by the Luide process as a bi-product in the manufacture of oxygen was tried in these experiments, but was found to contain so large a content of oxygen that it required a very careful treatment with hot copper to render it fit for use. The method of carrying on the absorption of the nitrogen by the strontium carbide was to heat the carbide in an electric tube furnace[1] by which the temperature can be regulated and maintained at the desired point. The carbide was placed in a porcelain boat, situated in the tube of the electric furnace at such a position that it nearly touched the junction of the thermocouple which was used to measure the temperature.

The nitrogen from the gasometer was dried over calcium chloride before entering the heated copper gauze, and was further dried by passing through two bottles containing sulphuric acid. The dried and purified nitrogen was then admitted to the tube of the electric furnace which was not heated until all the air had been displaced. The temperature was then raised so that the carbide was subjected to the required heating in an atmosphere of nitrogen.

In some of the experiments it was found better to introduce the carbide after the electric furnace had come to the required temperature.

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[1] **Tucker Electric furnace with Calorite resistors for the laboratory. Jour. Ind. & Eng. Chem. III 8, 595.**

In order to study the influence of pressure on the absorption a small steel tube was used[1] which had a tight fitting threaded plug at one end for the introduction of the sample contained in a small steel boat. A side tube provided means for the admission of the nitrogen which was raised to the required pressure by a force pump operated by hand.

The steel tube itself was of such size as to fit easily in the porcelain tube of the electric furnace. Before admitting the nitrogen the air was exhausted by a Geryk oil vacuum pump.

Analysis of the Product and Conclusions

The product obtained after treatment with the nitrogen was usually caked, the surface was white, another under portion brownish black to gray. The total nitrogen was determined by the Kjeldahl method.

In order to ascertain in what condition the nitrogen existed in the product the method of analysis recomended by N. Caro[2] was used.

This method consists in treating a sample of the product with excess of ammonical silver acetate solution, which precipitates silver cyanimid. The precipitate is washed free of ammonia and the nitrogen in it determined by the method of Kjeldahl.

The filtrate is then treated with caustic potash, and boiled to free the ammonia. The precipitate so formed is silver dicyanimid the nitrogen content of which is also determined by the Kjeldahl method.

For the cyanide the method of W. Feld[3] was employed which consists in boiling the sample with a strong solution of lead nitrate. The distillate is collected in caustic potash solution and the cyanide determined by titrating with silver nitrate using potassium iodide as indicator.

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[1] Tucker-Moody Jour. Am. Chem. Soc. XXXIII 9, 1483.

[2] Caro, Schuck and Jacoby, Zeit. angew. Chem. 23, 2405 (1907).

[3] Feld J. Gasbeleught 46.

The following results were obtained:

TABLE II

Influence of Temperature

No.	Temp. °C.	% N.	Time
1	500 °C	0.437	1 hour
2	800	1.297	1 "
3	1000	6.89	1 "
4	1000	0.76	1 "
5	1000	6.65	1 "
6	1150	8.60	1 "

Influence of Time

No.	Temperature	% N.	Time
7	1000 °C	9.08	3 hours

Influence of Pressure

No.	Temperature	Pressure lbs. sq. inch	% N.	Time
8	1000 °C	35	5.8	1 hour
9	1000 °C	45	5.27	1 "

From these results it appears that nitrogen is only absorbed by strontium carbide at fairly high temperatures which follows from Nos. 5 and 6, and that the influence of time is important as shown in No. 7.

Nitrogen under pressure is evidently without advantage for its absorption by this carbide.

The condition in which the Nitrogen exists in the Product

Analyses were made on several samples of the product as follows:

Total nitrogen #7 = 9.08%
Nitrogen as cyanimid = 2.25
Nitrogen as dicyanimid = .36
Nitrogen as cyanide = 5.90

Total nitrogen #3 = 6.89%
Nitrogen as cyanimid = 3.62
Nitrogen as dicyanimid = 0.24
Nitrogen as cyanide = 2.15

Total nitrogen #6 = 8.60%
Nitrogen as cyanimid = 3.19
Nitrogen as dicyanimid = trace
Nitrogen as cyanide = 1.54

These results while not entirely satisfactory show that some of the nitrogen is fixed by this carbide as cyanide which is quite different from the product obtained by the absorption of nitrogen by the carbides of calcium and lithium in which case the main product is cyanimid with only a trace of cyanide. We believe that the method of analysis particularly for the determination of the cyanide is not very accurate and that this accounts for the discrepancies particularly in product #6.

In conclusion we find that strontium carbide absorbs nitrogen at atmospheric pressure when heated to a temperature of from 1000° to 1200°C and that the product so formed contains an appreciable proportion of cyanide.

SOME FACTORS IN THE COST OF SODIUM HYDROCHLORITE PRODUCTION

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In the manufacture of bleaching liquor, or sodium hypochlorite, by the direct electrolysis of common salt the four more important factors entering into the final cost are labor, deterioration of apparatus, cost of salt consumed, and cost of power employed. Of these the first two, while important, are not subject to the variation incident to change in locality of the operation as are the last two, and are relatively constant. It is, therefore, to the relation of the cost of salt and cost of power as influenced by the conditions under which an apparatus may be operated that the present paper is devoted.

The experimental data employed were obtained from experiments made with an electrolyzing apparatus of the continuous flow type. It consisted of a rectangular trough divided into twenty-four compartments by bi-polar electrodes of graphite. The salt solution to be decomposed was fed continuously into one end of the apparatus passed successively between each pair of electrodes and exited at the opposite end. The electric current was supplied from a 110 volt lighting circuit, the amperes flowing depending upon the total resistance of the apparatus.

Since the salt solution as made up is used in its entirety for bleaching purposes however much or little of the salt therein contained may have been converted into the active bleaching agent, sodium hypochlorite, (in any case there being always a large excess of unconverted salt,) it is obvious that the less salt the solution contains per gallon the cheaper the resultant bleach solution will be. From this point of view, therefore, the apparatus should be fed with as dilute a solution of salt as will conduct the electric current through it. But on the other hand the more dilute the salt solution is, that is, the less salt it contains per gallon, the more electrical power will be required to form a given amount of sodium hypochlorite in it. It becomes important therefore to consider the relationship which exists between the strength of salt solution used, and the factors controlling the amount of electrical energy consumed per unit of sodium hypochlorite produced.

It can be shown that the cost of bleaching solution as measured by the cost of salt and electrical power consumed, is influenced by a large number of factors, and that not infrequently the maintenance of one condition will influence the cost in opposite ways. Summing up these factors their relationship may be expressed in a general way as follows:—

That increasing the amount of salt per gallon of salt solution used increases the total cost, because it,

1. Makes more expensive the first cost of the solution.
2. Causes a higher final temperature with heavy chlorate formation.
3. It increases the amount of current flowing and increases deterioration of electrodes.

It decreases the cost because it,

1. Lowers the resistance to the current and consumes less energy.
2. Decreases chlorate formation at the anode.
3. Increases production of cell.

A rapid rate of flow of solution increases the final cost because it,

1. Increases the consumption of salt.

It decreases the cost,

1. Because it maintains a lower temperature, and prevents chlorate loss.
2. It maintains a lower hypochlorite concentration and prevents reduction at the cathode.
3. It lowers chlorate formation at the anode.

Increasing the amount of available chlorine per gallon of solution increases the final cost because it,

1. Increases the reduction loss of the cathode.
2. Increases the oxidation loss at the anode.
3. Increases the temperature of outflowing solution.

But it greatly decreases the total cost, because it,

1. Makes more available chlorine per gallon effluent, and hence reduces the number of gallons of solution required for a determined amount of available chlorine.

It is apparent from the above considerations that if we use a large amount of salt, we will economize in electric power, and vice versa. The price which must be paid for salt and power varies at different localities, and the amount of salt and power which is most economical at one place may be the wrong amounts to use at another place where the costs are different. The question arises, therefore, how can the relationship between the cost of salt and cost of power be established, and how can such relationships be most conveniently expressed in order to be of general use?

Obviously from the complicated relationship shown above it will be necessary to make a great many experiments if we are to learn in a quantitative way how variations in the several factors effect the result. The following method was therefore developed, by which from the data from one experiment a series of results may be calculated.

The apparatus was equipped with thermometers, and means of withdrawing samples for analysis in the 4th, 8th, 12th, 16th, 18th, 22nd and end compartments. The run was commenced with a definite strength of salt solution, and the rate of flow was fixed as would give a strong bleaching solution in the last compartment. The current was allowed to flow for an hour or so, or until the apparatus came to equilibrium. That is, until the flow of current and the flow of solution into and out of the apparatus was constant, the temperature of the different compartments did not change, and the strength of available chlorine in the last compartment was constant. At this point the temperature in each cell was read, and a sample of the solution was taken from each of the cells equipped for the purpose, that is, 4, 8, 12, etc.

This sample and temperature represents the condition of the solution which would obtain if the apparatus ended with the respective compartments. That is, suppose the apparatus ended with the 4th compartment. Then the solution would leave it at this point and would have the temperature and composition of the sample taken from the compartment, when the current and rate of flow was as above given. This is true of the other compartments tested.

The complete data of such a run is given.

Run #20.

Sp. Gr. salt solution at 15°C. 1.0335 = 0.4 lbs. per gallon.
Average voltage 104.
Average current 39 amperes.
Rate of flow 11.5 gallons per hour.
Cost of salt per pound .5 cents.
Cost of power per K. W. H. 2 cents.
Temp. inlet solution 53.6°F.
Temp. outlet solution 125.6°F.
Temp. rise 72°F.

No. Cell	Temp. °F.	lbs. Cl per gal.	Current efficiency %	K.W.H. per lb. Cl.	lbs. salt per lb. Cl.	Cost power	Cost Salt	Combined Salt and power per lb. avail Cl.
4	69.8	.0178	60.5	2.44	22.5	.0488	.1125	.1613
8	80.6	.0294	50.2	2.94	13.6	.0588	.0680	.1268
12	95.	.0418	47.5	3.11	99.57	.0622	.0479	.1101
16	107.6	.0492	41.9	3.52	8.14	.0704	.0407	.1111
19	114.8	.0529	38.0	3.88	7.56	.0776	.0378	.1154
22	125.6	.0563	34.9	4.23	7.12	.0846	.0356	.1202
End	126.5	.0574	32.6	4.52	6.97	.0904	.0349	.1253

This table shows in the first column, how the temperature of the solution increased as it passed through the apparatus; the second, indicates the way in which the available chlorine is increased as measured in pounds per gallon. The third column gives the percentage of the current passing through which has been utilized in making the desired product, and it is seen to fall off as the end of the apparatus is reached. The power consumed per pound of available chlorine produced therefrom increases, while the amount of salt used per pound of available chlorine decreases as the solution becomes stronger in its bleaching power. This is true also of the cost of the two elements.

Following the explanation above given we see that if the apparatus ended with the 4th compartment, and was fed with salt solution containing four-tenths pounds per gallon, at the rate of 11.5 gallon per hour, a current of 29 amperes would pass through, and the outflowing bleach liquor would be at a temperature of 69.8°F, and would contain .0178 lbs. of available chlorine per gallon. The current efficiency would be 60.5% and the total cost per pound of available chlorine provided would be .1613 cts. If the apparatus ended with the 12th compartment the table shows the values which would here be obtained and so on.

It is seen therefore, that under the condition of cost of salt and power, strength of salt solution and rate of flow, as here obtaining it would be cheapest to stop the operation at the 12th compartment, where the available chlorine produced cost \$.1101 per pound. Beyond this point as the solution passed through the apparatus more hypochlorite is formed, but the expenditure for power is so large owing to chlorate formation and cathode reduction as compared to the saving in salt and the net cost of available chlorine produced becomes larger as we pass beyond the 12th compartment.

But since the apparatus is of 24 compartments designed to operate on a current of 110 volts, in order to use an apparatus of the size represented by the 12th compartment we would require a generator furnishing twelve twenty-fourths of 110 volts, or 55 volts. Since we are *limited* to a current of 110 volts, the question arises how can we vary conditions so as to have the *entire* apparatus operate so that the yield of available chlorine, current efficiency, and cost of materials will be the same at the end of the 24th compartment as it was in the experiment at the 12th compartment or at any other selected compartment? The answer may be found in the following considerations:—

Let us assume that in an experiment as above described it was found that available chlorine was produced at the lowest price in the 12th compartment. It would be impossible to allow the apparatus to empty at this point and pass the current through but twelve compartments, because the voltage of the line being 110, the resistance would be ½ too low in but 12 compartments, and twice too much current would pass. An external resistance of any form equivalent to 55 volts could be inserted, but the energy consumed by such resistance is total waste, so far as making available chlorine is concerned. Instead of a resistance of 55 volts, however, we can put another apparatus in exactly like the first 12 compartment one and hence use the current at 110 volts as furnished from the line. This apparatus would be fed with the same strength brine at the same rate, and the result would be that we would get the same results of minimum cost in both pieces of apparatus, use the entire energy of the line and produce twice as many gallons of bleaching solution.

Now practically this same result may be accomplished if we used the original apparatus with the 110 volt current, and run the salt solution through *twice as fast* as in the experimental run. While the additional rate of flow would of course maintain a lower temperature, and hence a somewhat smaller number of amperes would flow through the apparatus, the loss of hypochlorite through reduction would be greater, inasmuch as that made in the first compartment is subjected to the cathodes of the following compartments, and the concentration of the hypochlorite would also increase more slowly and hence the loss would be correspondingly smaller.

Hence if by such an experimental run it is found that available chlorine can be produced cheaper after the solution has passed through any given number of compartments, N, at the rate of flow of R gallons per minute, the rate X at which the solution must flow through the entire 24 compartments of the apparatus to get the same cost per pound is given by the proportion:

N	24	R	X
The number of compartments in experimental run giving minimum cost.	The entire apparatus.	The rate of flow during experimental run.	The required rate of flow through entire apparatus.

To test the validity of this method two runs were made with a 5% brine, one at the rate of 35 liters per hour and another at 70 liters per hour. According to the above reasoning the results obtained at cell #12 in the first run should be the same, within the limits of experimental error, as the results at the end of the apparatus when the rate is twice as fast. The following values were obtained:—

	Results at compartment #12	Results at end of apparatus
Rate of flow liters per hour	35	70
Grams chlorine per liter...	3.7	3.8
Temp. Rise.............	15°C	15°C
Current efficiency.......	45.6%	46.8%
Cost per kg. Chlorine.....	$.270	$.271

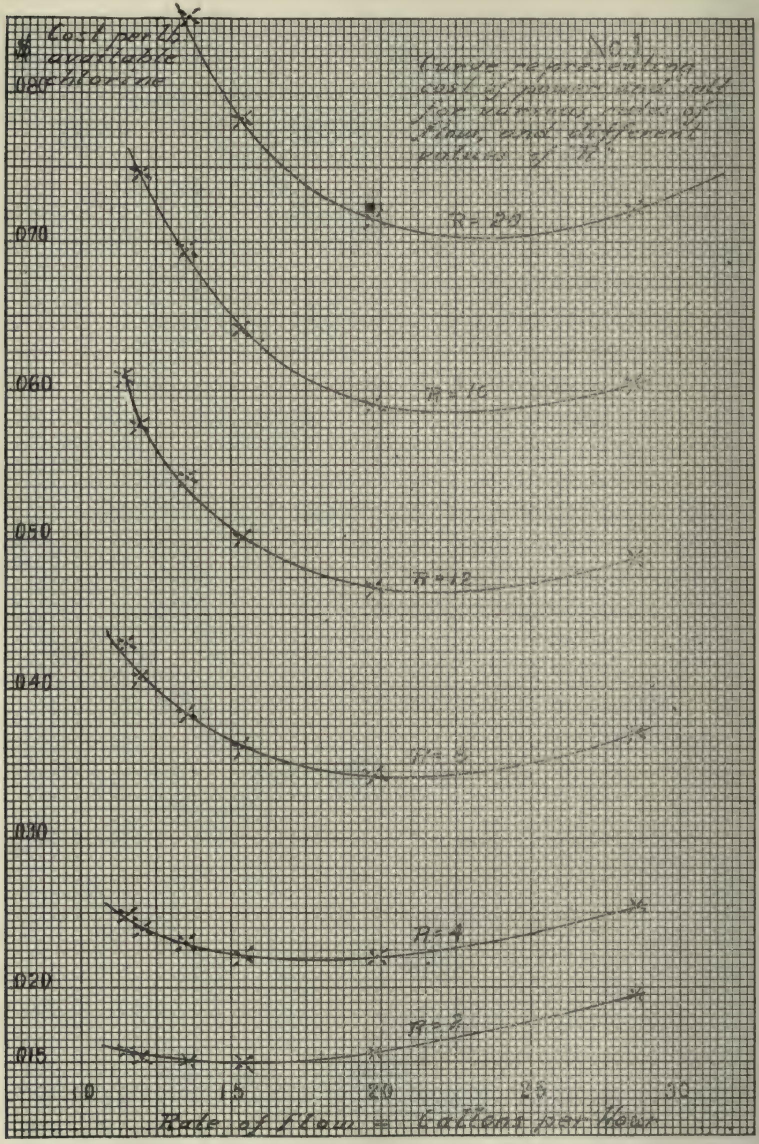
The figures show a satisfactory check on the method.

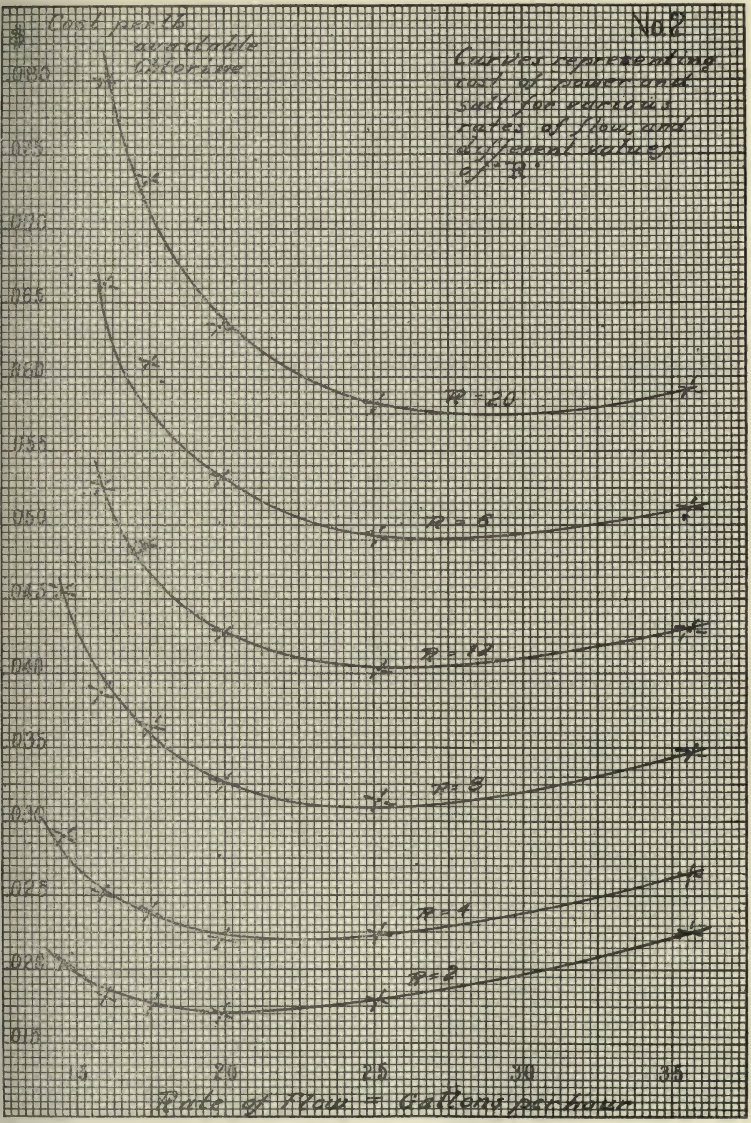
Cost Ratio. The combined cost of salt and power may be expressed as a ratio of one to the other. Thus if the cost of power per K. W. H. is 2 cents and the cost of salt is .5 cent per pound, the ratio is 2 divided by .5, or 4. That is, power is four times as expensive as salt in their respective units. By taking one of these factors as unity, we may construct a table showing the relation between the rate of flow of any given brine through the apparatus and the combined cost at any ratio of cost of salt to cost of power. This is given on chart No. 1 for a 10% salt solution, or about 91 pounds per 100 gallons. The cost figures are based on salt at .1 cent per pound. Thus the bottom curve labeled R=2 means when power costs twice as much as salt. If salt costs one-tenth cent per pound, the relation between rate of flow and cost may be read off directly: but if salt is .5 cent per pound (which would mean that power is 1 cent per K. W.H., since the ratio is 2) the combined cost would be just 5 times the figures given as ordinates. Suppose we have a locality where salt is .3 cent per pound and power is 3.6 cents per K. W. H. This is a ratio of 12. Looking at the curve marked R=12 we find that the lowest cost is at a rate of 25.5 gallons per hour. The cost corresponding to this is .041 dollars. But this figure is for salt at .1 cent per pound. Since at the locality in question salt is .3 cent per pound the cost would be three times this $.123, or 12.3 cents per pound of available chlorine. In a similar way we find from Chart No. 2 for a 5% brine the rate of flow showing the minimum cost is 22.5 gallons, and the combined cost is $.138.

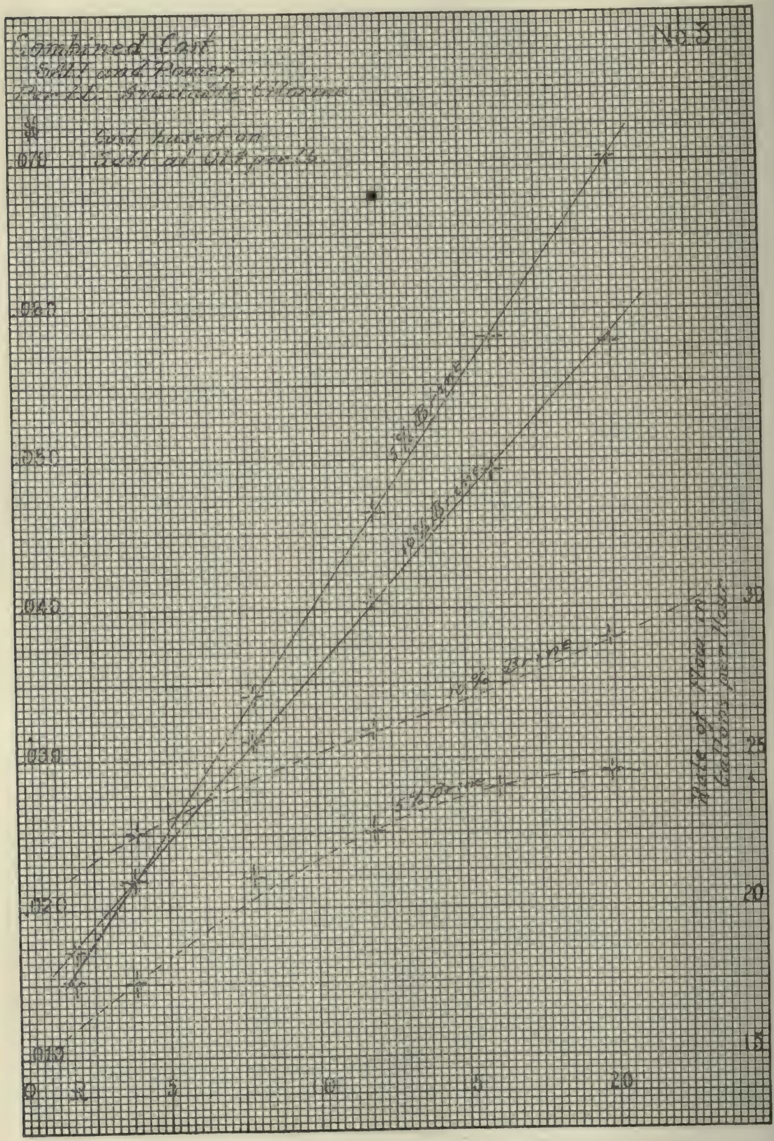
By combining the minimum cost points of all three curves and the corresponding rates of flow we have produced Chart No. 3 which contains the final working curves. The solid curves show the minimum combined cost based as before on .1 cent per pound of salt, in its relation to R, the ratio of cost of power per K. W. H. to cost of salt per pound. The dotted curves show the mean rate of flow to produce the minimum cost for the 5% and 10% brine.

The solid curves cross each other at a ratio of about 4. This means that in general where power is less than four times as expensive as salt it is cheaper to use a 5% brine or about 40 pounds salt per 100 gallons: otherwise a higher concentration up to 90 or 100 pounds salt per 100 gallons is cheaper. If the cost of power is much greater than twenty times that of the salt an apparatus of the type used here is inadvisable since it will not run much faster than 30 gallons per hour at best. In this connection it must be mentioned that, although the cost for salt and power using a 10% brine is lower where R is greater than 4, the current density is considerably higher with the more concentrated solution and the cost for renewal of electrodes would be greater.

Such curves as these are all that are necessary to determine the strength of brine and the rate of flow which it is advisable to use in any particular locality with an apparatus of the type here used to obtain a minimum cost for available chlorine, as soon as the cost of salt and power is known for that locality.


No. 1
Curve representing cost of power and salt for various rates of flow, and different values of "R"
$ Cost per lb available chlorine
.080
.070
.060
.050
.040
.030
.020
.015
R = 20
R = 16
R = 12
R = 8
R = 4
R = 2
10
15
20
25
30
Rate of Flow = Gallons per Hour


$ Cost per lb available Chlorine
No2
Curves representing cost of power and salt for various rates of flow and different values of "R"
.080
.075
.070
.065
.060
.055
.050
.045
.040
.035
.030
.025
.020
.015
R = 20
R = 6
R = 12
R = 8
R = 4
R = 2
15
20
25
30
35
Rate of Flow = Gallons per hour


Combined Cost
Salt and Power
Per lb. Available Chlorine
$
Cost based on
Salt at
No. 3
.070
.060
.050
.040
.030
.020
.010
0
2
5
10
15
20
5% Brine
10% Brine
10% Brine
5% Brine
Rate of Flow in Gallons per Hour
30
25
20
15

THE DETERMINATION OF OXYGEN IN IRON AND STEEL BY REDUCTION IN AN ELECTRIC VACUUM FURNACE

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At the fifth meeting of this Congress held in Berlin in 1903 F. Lurman presented a paper on the determination of oxygen in iron and steel in which he pointed out the necessity of a new method which would measure the total oxygen in the sample, and especially that portion which is combined with manganese, aluminium, silicon, and the other oxides not reducible with hydrogen. Since that time no advance has been made in this important field of metallurgical work.

The important role which the oxides of iron and the other metals play in determining the physical and chemical properties of iron and steel was first clearly brought out by Prof. Ledebur in 1882. At this time Ledebur proposed the analytical method for determining oxygen which bears his name and which is based upon the reduction of the oxide at a red heat by hydrogen, and weighing the water thus formed. Owing to the fact that at a high temperature hydrogen reduces only the oxides of iron leaving unattacked to a large extent the oxides of manganese, aluminum, silicon, titanium, etc., it is obvious that the method is not a satisfactory one, although up to the present the only one available for the purpose.

Other methods have been proposed for determining the oxygen in iron and steel based upon the solution of the constituents not oxides. As examples may be mentioned the method of dissolving the sample in ethereal solutions of iodine or bromine: or that based upon the volatilization of the iron in a stream of chlorine gas at a high temperature: but none of these methods have proven of any value.

Although the detrimental effect of combined oxygen in iron and steel has been known since the time of Ledebur's first paper, it is only within the last few years that the full significance of these effects has been appreciated. That iron oxide can exist in iron and steel in more than one form seems certain, and that the oxides of the different metals associated with the iron should have characteristic effects is surely to be expected. But in the absence of any satisfactory analytical method for determining the oxide present, the relation between cause and effect has been of necessity a most imperfect one. It is hoped that the method of determining oxygen now to be described will be an aid in establishing the connection between the oxygen content and the physical and chemical properties of iron and steel.

In the now well known reaction wherein the oxides of the elements are converted into the corresponding carbides by heating them with an excess of carbon to a high temperature in an electric furnace, the oxygen is given off quantitatively as carbon monoxide. The quantitative formation of carbon monoxide is aided by an excess of carbon at high temperatures, and by a low pressure: also, as has been pointed out by Moissan, the refractory oxides are more readily reduced in the presence of metallic iron.

The details of the method as at present worked out are as follows:—

A vacuum furnace of the Arsem type as supplied by the General Electrical Co. is employed, and is shown in Fig. 1. The gun metal chamber (A) of the furnace of 20 capacity rests inside the waterjacket (R). The cover (B) is fastened to the chamber by means of 18 cap screws (D), and the joint is made tight by a rigid lead gasket. The tube (J), through which the air is exhausted is soldered into the cover. The window tube (G) is fastened to the cover by six cap-screws, the joint made tight by another lead washer. The mica window (E) is placed in the top of the window tube. Current is lead in through the electrodes (W), which are brass tubes containing running water. The graphite heater (L) is fastened to the electrodes by means of the clamps (U). The crucible is supported by the stand as shown in the figure and is thus placed in the hottest part of the furnace.

Twenty to twenty-five grams of the sample of metal in which the oxygen is to be determined is placed in a small graphite crucible and about four or five grams of finely powdered graphite added. The crucible is then placed in the furnace, the cover bolted down, and by means of a small rotary oil pump operated in series with a Geryk pump a vacuum of .01 of a mm. is obtained in the furnace in less than fifteen minutes. After thoroughly exhausting the furnace, the cooling water is turned on and the crucible and contents heated to about 500°–600° with the pump still running. This is necessary in order to pull away as completely as possible the oxygen absorbed by the heater and crucible. As carbon does not begin to reduce the oxides below 900° there is no danger in heating the crucible up to 500°. After fifteen minutes the furnace is allowed to cool, which it does very rapidly. Nitrogen that has been dried over sulphuric acid and phosphorous pentoxide is now allowed to enter the furnace until the latter is about half full. This is then pumped out and the crucible again gently heated. Only by such a treatment is it possible to reduce the oxygen left in the furnace to a reasonably small value. It seems impossible to pump the absorbed oxygen entirely out of the furnace, but by washing with dry nitrogen it can be almost eliminated.

The stopcock leading to the pump is now turned off and seventy volts applied to the electrodes which causes a current of about 200 amperes to flow through the heater. A high temperature is reached very rapidly, the metal melting in three or four minutes. Just as the metal melts violent ebullition very often occurs. This is prevented by opening the circuit for a short time and allowing the charge to cool. The metal soon becomes quiet and the heating is continued for twenty minutes. The furnace is then allowed to cool thoroughly, after which fresh air, or better nitrogen, that has been dried over sulphuric acid and phosphorous pentoxide is allowed to completely fill the furnace.

The gas now in the furnace is analyzed for carbon monoxide in the following manner:

The vessel C in Fig. II is exhausted by means of a Toepler pump, and connections made with the furnace as shown in the diagram. The stopcock from the furnace is opened and if the gas in the furnace is under a pressure other than atmospheric, the difference is shown by the differential gauge E. Correcting the barometric pressure by this amount gives the pressure of the gas inside the furnace. Stopcock F is now opened and the vessel and the pump filled with gas. A decrease in pressure corresponding to the volume of gas taken from the furnace is shown by the gauge E, and we are thus able to calculate the fraction of gas taken from the furnace. By this method we are practically free from any errors due to temperature variation.

The gas is now slowly forced over iodine pentoxide which is heated to 130°C. and here the carbon monoxide is oxidized to carbon dioxide liberating an equivalent amount of iodine. The latter is absorbed in a 10% solution of potassium iodine and subsequently titrated with N–100 sodium thiosulphate.[1]

A much more simple method of withdrawing an aliquot part of the gas for analysis, if a large quantity of mercury is available, is to use a mercury aspirator instead of the Toepler pump. By replacing the reservoir C by a liter bottle which may be filled with mercury, a known fraction of the contents of the furnace may be withdrawn, and forced directly through the iodine pentoxide tube.

The first point to be definitely determined was, how free from oxygen can the furnace and its heating element be made: in other words, using a sample of iron known to be free from oxygen, what amount of oxygen will be shown in a blank experiment? It was found that the oxygen indicated by the iodine liberated from the iodine pentoxide was due to three factors: first, a certain practically constant amount of iodine set free from the iodine pentoxide when air or nitrogen free from carbon monoxide was led over it, second, the actual oxygen absorbed on the walls and on the heater of the furnace, third, the moisture in the furnace.

That iodine pentoxide when heated to 150° in a current of dry air or nitrogen would give up small amounts of iodine has been recognized by previous investigators. (L. A. Levy, Soc. Chem. Indust. 30, 1437) We have found that by reducing the temperature to 130° the oxidation of the carbon monoxide is complete, while the decomposition of the pentoxide is reduced to a minimum. By withdrawing from the furnace at each analysis a constant volume of gas and drying the same over phosphorous pentoxide, a uniform blank amounting to .006 grams oxygen for the furnace contents was obtained. The weight of oxygen absorbed on the walls of the furnace and in the heater when a vacuum of .01 mm. was maintained was found in blank analysis using iron free from oxygen to be .02 grams. If the air used to dilute the furnace contents previous to withdrawing the sample of gas for the carbon monoxide determination be not dried over phosphorous pentoxide, the amount of oxygen indicated may rise to .035 grams. By first exhausting the air from the furnace, and then filling with nitrogen and re-exhausting the amount of oxygen shown by a blank analysis was found to be between .0120 and .0129 grams.

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[1] **Nicloux and Gautier, Compt. Rend. 126, 746.**
Kinnicut and Sanford, Jour. Am. Chem. Soc. 22, 14.

The accuracy of the method so far as the ability to carry out the operations without introducing errors not corrected for as above was shown by the fact that a sample of iron or steel containing oxygen may be heated, and the oxygen determined: upon reheating the same charge with additional carbon no further formation of carbon monoxide is obtained.

To determine the accuracy with which the oxygen of a sample of iron or steel will be converted to carbon monoxide, a number of analyses were made using an iron of very low oxygen content, and adding known quantities of the various oxides in the pure form. In addition to iron oxide, only the very refractory oxides of aluminium and silicon were used: other easily reducible oxides such as manganese and copper will introduce no difficulties. The weighed amount of the pure oxide together with a known weight of iron was placed in the graphite crucible and covered with powdered graphite and heated as described. From the oxygen as determined was subtracted that due to the blank and the iron and the following results were obtained.

	Weight of Oxide	Oxygen Calculated	Oxygen Found
Ferric oxide	.5650	.1695	.1700
" "	.6525	.1960	.1940
" "	.8400	.2520	.2440
" "	.1516	.0455	.0480
Aluminium oxide	.4925	.2310	.2040
" "	.1860	.0875	.0810
" "	.3065	.1440	.1260
Silica	.0673	.0360	.0342
"	.0320	.0181	.0171

While the results as obtained are not so accurate as is desired, the reduction being somewhat incomplete, and therefore the results uniformly low, the method has served to explain the discrepancies noted between the oxygen content as determined by the Ledebur method in certain samples and their physical and chemical properties. As examples of such analyses may be mentioned the following.

Sample No. 1 is a special heat of an open hearth steel to which iron ore and an excess of manganese was added in the ladle. The finished steel gave every evidence of having a high oxygen content, although, by the Ledebur method, but .006% oxygen was obtained. When determined by the vacuum furnace reduction method the real oxygen content of the steel proved to be .20%.

Sample No. 2 is a high grade of open hearth steel in which the Ledebur method detected no oxygen. The vacuum method showed that there was .09% present.

Samples No. 5 and 6 represent two ingots from the same heat of open hearth steel of high quality. To No. 5 was added some iron oxide as the ingot was poured. The oxygen content of the ingot giving satisfactory results was .065% while that to which the ore was added and which was highly unsatisfactory proved to be .31%.

Nos. 11a and 11b are duplicate analyses of an ingot iron of early manufacture. The vacuum furnace method indicates about three times as much oxygen as the Ledebur method. 12a and 12b is ingot iron of later make and show an oxygen content of but .10%. The full analyses are given in the following table.

No. 1 Open hearth steel to which manganese and ore was added.
No. 2 Good quality of open hearth steel.
No. 3 Open hearth steel.
No. 4 Same heat as No. 3 but from ingot to which ore was added.
No. 5 Open hearth steel. Ore added to ingot.
No. 6 Same heat as above. No ore.
No. 7 Open hearth steel.
No. 8 Open hearth steel.
No. 9 Open hearth iron.
No. 10 Open hearth iron.
No. 11a Ingot iron. Early manufacture.
No. 11b Ingot iron. Early manufacture.
No. 12a Ingot iron.
No. 12b Ingot iron.

No.	C	Mn	S	P	Si	Cu	0 Ledebur	0 Vacuum Furnace
1	.19	.92	.052	.123			.006	.29
2							.000	.09
3	.17	.65	.097	.064	.017			.11
4	.12	.17	.065	.088	.015			.33
5	.09	.18	.061	.087	.019			.31
6	.14	.24	.070	.092	.009			.065
7	.09	.33	.065	.068	.006	.17	.009	.021
8	.08	.33	.036	.070	.005	.22	.010	.039
9	.01	.03	.050	.007	.003	.20	.037	.056
10	.01	.04	.015	.008	.004	.19	.052	.064
11a	.01	trace	.015	.002			.069	.23
11b	"	"	"	"			.076	.21
12a	.02	.03	.029	.004	.0014	.043		.10
12b	"	"	"	"	"	"		.11

It is intended that this paper be considered a preliminary communication, and it is hoped that the method will be both simplified and improved by further work. It is published at this time in the hope that others interested in the effect of oxygen on steel will find in the idea something of value.

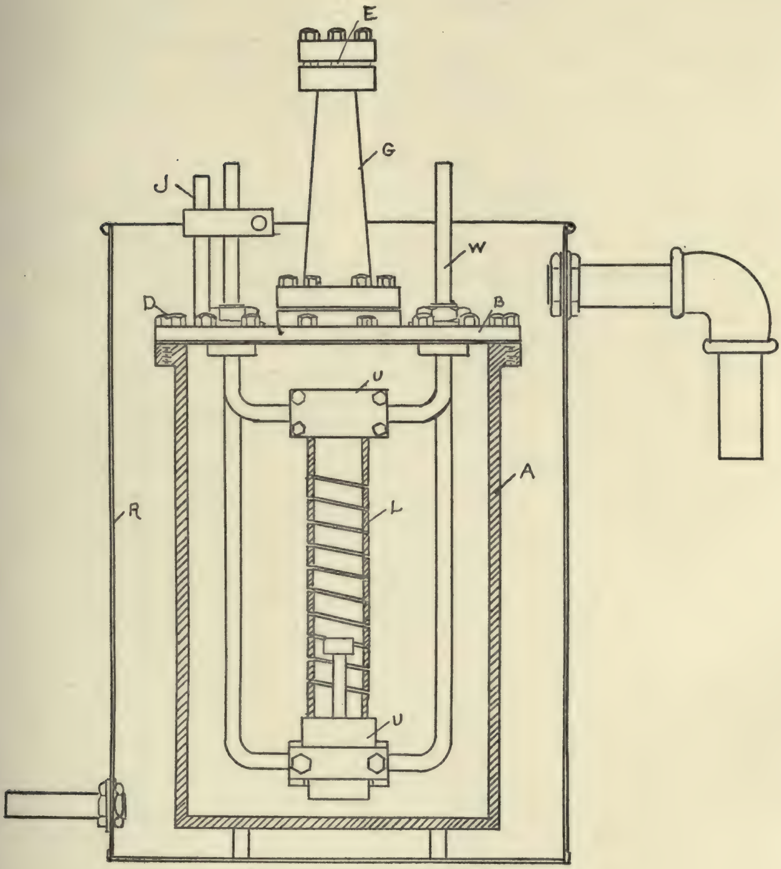

Fig. I

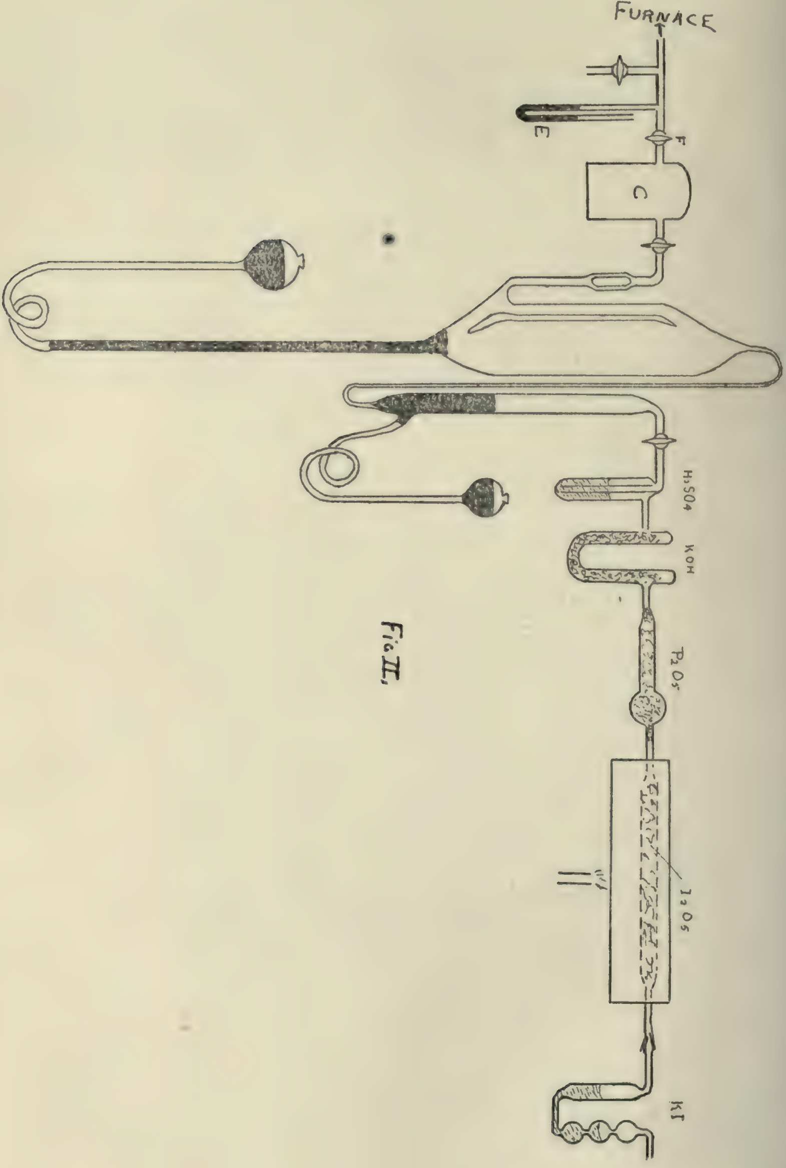

Fig. II,

MINERAL ELECTRODES

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1. INTRODUCTION

It is generally known that pyrolusite, magnetite, and pyrite are conductors of electricity but it does not seem to have been recognized that a number of other sulphides are even better conductors than pyrite and can consequently serve as electrodes. The object of this preliminary paper is to set forth some of the phenomena which have been discovered to occur when conducting minerals function as electrodes in aqueous solutions.

The minerals studied, in the approximate order of their conductivity, are galena, pyrrhotite, magnetite, chalcopyrite and pyrite. These substances are attackable in various degrees in the process of electrolysis, depending upon whether they function as cathode or anode. As voltaic electrodes some of them develop potentials which are comparable with those shown by the metals in contact with solutions of their salts.[1]

2. ELECTROLYSIS

Sodium carbonate was electrolyzed for 5 hours with a current of 0.04 amperes, using electrodes of pyrite. As cathode, the pyrite remained bright and lost only 0.0025 g. Hydrogen was evolved with a trace of hydrogen sulphide. As anode the pyrite became coated with yellow hydroxide of iron, the gas evolved was less, after drying the electrode showed a loss of 0.0495 g.

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[1] Suggestions of these facts are found in the following papers: R. W. Fox. The Electro-Magnetic Properties of Metalliferous Veins in the Mines of Cornwall. Phil. Trans. 1830, Pt. 1, 399–414. W. Skey. On the Electromotive Power of Metallic Sulphides. Trans. and Proc. New Zealand Institute 3, 232–236 (1871). Carl Barus. The Electrical Activity of Ore Bodies, in "Geology of the Comstock Lode" by George F. Becker. U. S. Geological Survey, Monograph 3, 309–367 (1882). V. H. Gottschalk and H. A. Buehler. Oxidation of Sulphides. Economic Geology, 7, 15–34 (1912).

and sulphate was formed in the solution. It was attempted to oxidize the sulphur in a small quantity of finely ground pyrite in the bottom of a platinum dish by making it anode in a sodium carbonate solution but the powder was not attacked as well as the large crystal had been. In nitric acid the behavior of pyrite as cathode and anode was similar altho the cathode showed a slightly greater loss, 0.0098 g. to 0.0715 for the anode.

It is very easy to precipitate copper, iron or other metal upon cathodes of pyrite. If pyrite is made anode in copper sulphate solution black copper sulphide is formed and clings to the electrode. What is rather remarkable, pyrite remains almost unchanged in weight and lustre as anode in ferrous sulphate solution, which seems to be due to the electrolytic regeneration of the pyrite as fast as it is decomposed.

In sodium polysulphide solutions it is again chiefly the anode of pyrite which loses in weight.

Magnetite shows very little change in weight as cathode; as anode it gains slightly. As a matter of fact, magnetite has been employed commercially in large electrodes so it is superfluous to describe its behavior.

Galena as cathode suffers some mechanical disintegration along cleavage planes but the chemical attack is slight. The anode becomes covered at first with lead sulphate and eventually with lead peroxide, with a marked gain in weight.

Anodes of Graphite are said to be much more oxidizable in acid solutions than in alkaline solutions.

3. ELECTROMOTIVE FORCE MEASUREMENTS

The potentials shown by these electrodes against various solutions depend partly upon the specimen used, but to a much greater degree upon the nature of the solution. As a preliminary basis of reference they were measured against normal potassium chloride solution, using a normal calomel electrode as the other half electrode. Since the potentials after the specimens are treated with acids or alkalies do not immediately return to their initial value the best values would seem to be those shown by fresh specimens. A list of values obtained from fresh specimens is given in Table 1. The measurements were made by the usual compensation method of Poggendorff with Lippmann electrometer as indicating instrument. The single potentials were computed by adding (or subtracting) the value .56 volts from the total measured voltage.

TABLE 1

Single Potential of Electrode to $\frac{N}{1}$ KCl.

Pyrolusite	+0.93
Pyrite	0.90
Marcasite	0.72
Pyrrhotite	0.56
Magnetite	0.40
Galena	0.38
Commercial FeS	−0.03

Chalcopyrite and chalcocite fall between marcasite and galena. The above order is consistent with the fact that marcasite is more easily oxidized than pyrite.

Most specimens of pyrite gave potentials ranging from 1.01 to 0.76, altho one specimen went as low as 0.56. Marcasite showed values from 0.56 to 0.83. This difference would therefore appear to be a quick means of distinguishing pyrite from marcasite. A nodule found at a depth of 7 feet gave 0.87 and was therefore mostly pyrite. The variations of several of these specimens from day to day (out of the solution) is shown in Table 2.

A change in the electrolyte affects the potential of these electrodes markedly, especially a change in the acidity or alkalinity of the solutions.

Pyrite and marcasite are most positive in acid solutions. Their potentials fall as the solutions become alkaline and they may even become negative in alkaline sulphide solutions. For example a certain specimen of pyrite gave +0.95 volt in $\frac{N}{1}$ H_2SO_4, 0.80 in $\frac{N}{1}$ KCl, 0.14 in $\frac{N}{1}$ NaOH and −0.17 in $\frac{N}{1}$ Na_2S.

Galena, similarly, gave 0.32 in $\frac{N}{1}$ H_2SO_4, 0.28 in $\frac{N}{1}$ KCl, 0.11 in $\frac{N}{1}$ NaOH, and −0.19 in $\frac{N}{1}$ Na_2S.

Fresh chips of magnetite gave about +0.40 volt against $\frac{N}{1}$ KCl, 0.94 in $\frac{N}{1}$ H_2SO_4 and −0.22 in $\frac{N}{1}$ NaOH.

In alkaline sulphide solutions the potentials are far more constant and reproducible than in acids or salt solutions but there is not as much difference between the values for the different sulphides. Moreover there is very little difference between values shown by Na_2S and $Na_2S_{4\cdot5}$. Thus in $\frac{N}{1}$ Na_2S galena gave −0.19, pyrite −0.17, artificial FeS −0.17, pyrrhotite −0.09 and marcasite −0.07. In $\frac{N}{1}$ $Na_2S_{4\cdot5}$ galena and pyrite gave −0.16 and marcasite −0.07. The same specimen of pyrite after washing with water gave +0.36 in $\frac{N}{1}$ KCl, after dipping in acid, cleansing, and replacing in $\frac{N}{1}$ KCl +0.74, and finally when replaced in Na_2S −0.17, the previous value. It may be that these potentials in alkaline sulphide solution represent fewer phases, as for example pyrite and FeS and no others. The values in Na_2S are evidently more reproducible than those in KCl.

TABLE 2

Variations of Potential with Time, $\frac{N}{1}$KCl.

	1	2	3	4
April 11	1.01	0.96	0.94	0.72
May 4	0.99	0.92	0.88	0.71
June 14	0.93	0.88	0.87	0.68
" 18	0.94	0.88	0.85	0.83
" 25	0.97	1.00	0.83	0.56

1. Pyrite collected by A. A. Julien (No. 39).
2. Pyrite from Elba.
3. Octahedron of Pyrite, French Creek, Pennsy.
4. Marcasite, coxcomb, collected in Missouri by C. E. Siebenthal.

4. THEORY

From facts so far obtained it seems difficult to characterize these electrodes. At first thought one might decide to class them in the group of metallic electrodes having a very insoluble depolarizer but the direction and value of their electromotive forces do not correspond to that view. In most solutions the electrodes are positive, tending to react chemically with positive ions to form oxides or sulphides while the positive charge passes from the ion to the electrode thus constituting the current over the wire to the other electrode. It would accordingly be appropriate to term them *oxidizing* or *sulphidizing* electrodes. On the other hand, the great effect of alkalinity or acidity upon their potentials suggests that they may function in part as oxygen (or hydrogen) electrodes and it seems reasonable to conclude that the high potential of oxygen might interfere with the lower potential of sulphur even when sulphur was present in excess. Finally in alkaline sulphide solutions the electrodes become negative, the tendency is for sulphide ions to discharge and the electrode becomes a *reducing* one.

It appears strange to class sulphides with oxidizing substances but that is where they fall for the most part according to the potential criterion; on the other hand the nature of the solution evidently determines the classification since in alkaline sulphide solutions they are negative and hence become reducing electrodes.

With oxides one can reasonably hope to obtain reversible electrodes because the intermediate substance, water, does not escape. With sulphides the chief conditions of reversibility would appear to be to maintain a supply of sulphide either as alkaline sulphide or as an insoluble metallic sulphide. These matters will require much further experimental work for their complete elucidation.

In electrolysis these minerals may even function in some degree as unattackable electrodes. Evidently the time factor here does not permit equilibrium conditions to be rapidly obtained so that hydrogen or oxygen is evolved more easily than the electrode is decomposed. As has been pointed out, a moderate current evolves chiefly hydrogen from a pyrite cathode whereas the equilibrium probably corresponds to the formation of hydrogen sulphide.

The sulphides of low potential convert ionized hydrogen into hydrogen sulphide spontaneously, galena barely gives a test for hydrogen sulphide with dilute acids, while marcasite and especially pyrite are very stable in acids. The explanation of these facts is not obvious, for the differences in simple solubility are not great.

The electromotive forces under discussion are probably the cause of such earth currents as have been noted in mines. Moreover, surface solutions are usually acidic, deep solutions neutral or alkaline which would cause currents in veins to flow downward through the solutions and upwards through mineral deposits corresponding with the observation made by Fox in the mines of Cornwall. Whenever single crystals of pyrite are bathed by a solution of gold, a metal of low electro-affinity, local electrical action must tend to cause the deposition of the gold. This may be one reason for the frequent association of gold and pyrite.

Pyrite in contact with acid solutions must protect itself from oxidation by its own electrical polarization (or by a film of hydrogen) and the other sulphides must act similarly tho in smaller degree, so that with two sulphides in contact the one of lower potential will act as anode to the others and hence, as has been pointed out, undergo oxidation first. The fact of this increased oxidation of one sulphide in contact with another was noted in chemical studies by Gottschalk and Buehler before they developed an explanation in terms of electrical action.

MILL SCALE AS A CAUSE OF THE PITTING OF STEEL PIPES

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Steel seems destined to come more and more into use as a material for the construction of water conduits of certain size. For small pipes, say up to a diameter of about three feet, cast iron has proved most satisfactory and economical. As the size increases above this point, cast iron meets a formidable competitor in steel, for although this metal costs more than cast iron, it is stronger and the pipe may be thinner. The use of steel is increasing and it would increase more rapidly if engineers did not fear that corrosion would limit the life and perhaps cause the failure of the pipe line. Cast iron has been tried for many years and experience has shown that it has a long useful life, that may be depended upon. Some wrought iron pipes also have lasted well. Steel pipes have been used for a shorter period. In general they too have retained their useful life, although in some cases, where they have been exposed to exceptionally severe conditions, they have given trouble. A number of steel pipe lines have developed leaks, due to the corrosion of the metal in spots, that is to pitting. In this respect steel appears to differ from wrought iron, over the surface of which the rusting is more uniform. In fact it is this tendency to pit that engineers chiefly fear. Steel pipes almost never fail completely by breakage, as cast iron pipes sometimes do; they merely leak through the small holes or pits produced by corrosion, so that failure would come about as a gradual process. Nevertheless, leaks are always undesirable and many leaks, or a large leak, may be serious.

The general subject of the corrosion of steel has been carefully considered during the last few years and the relative advantages of different grades of steel and iron have been much discussed by engineers, chemists and manufacturers. Some have claimed that wrought iron and steel were equally durable; some have claimed decided advantages for that form of mild steel known as American ingot iron, on account of its low manganese content and the general resemblance of its chemical analysis to that of wrought iron; while some have claimed that the presence of small amounts of copper in steel tended to make it resist corrosion. In these discussions the importance of one factor has been very largely overlooked, namely, that of the mill scale, and as far as the use of steel for pipe lines is concerned, attention has been diverted from an important element of the problem. Although it is generally accepted by text book writers that pitting is closely connected with the presence of mill scale and that steel from which mill scale has been removed does not pit, the salesmen of the steel companies and even the chemists themselves have much to say about the absence of manganese and the presence of copper, and very little to say about the nature of the mill scale or whether this scale is or is not affected by the purity of the metal. It is to call attention to this neglected phase of the subject that the present paper has been prepared.

Occasion of the Investigation

In November, 1911, Mr. E. A. Fisher, City Engineer of Rochester, N. Y., requested one of us to undertake an investigation to ascertain the relative merits of steel, American ingot iron and wrought iron, for the construction of a 66-inch sewer outlet 9,000 feet long into Lake Ontario. This pipe is to carry the effluent from sedimentation tanks through which the sewage of the city is to be passed before being discharged into the lake at a point 7,000 feet from the shore.

Through the courtesy of Mr. Emil Kuichling, Consulting Engineer to the City of Rochester for this project, samples of steel, wrought iron and ingot iron were secured from the Allegheny Steel Company. Later, through the courtesy of Mr. C. F. W. Rys, Metallurgical Engineer of the Carnegie Steel Company and Mr. V. Browne and T. G. Siexas of the Allegheny Steel Company, samples of steel containing known amounts of copper were secured. Other samples were obtained at various places.

Nature of the Experiments

At the beginning a few simple immersion tests were made. Samples of the steel and iron were placed in jars of distilled water, Brooklyn tap water, salt solutions, solutions of chloride of lime, dilute acids, strong acids, etc., and observations and analyses made to determine the relative amounts of corrosion of the different samples. The results were of some interest, as noted below, but practically speaking it was found that they could not be relied upon to tell which metal would act best when submitted to the conditions expected at Rochester. The immersion tests in tap water and dilute solutions progressed too slowly, while the use of strong solutions failed to reproduce in the laboratory the conditions that would be met in actual practice. Difficulties also arose in controlling the oxidation of the iron in the solutions after it had been dissolved in the ferrous condition. This was influenced by the volume of the solution used, the ratio of the volume to the surface of water exposed to the air, and several other factors, as Friend has well shown in his recent book on The Corrosion of Iron and Steel.

Finding that the ordinary accelerated tests, using strong acids, were unreliable so far as the problem at hand was concerned, a different kind of accelerated test was tried, namely, one in which corrosion was stimulated by a current of electricity; that is, an electrolysis test. This was not employed for the purpose of observing those phenomena of corrosion that ordinarily occur when stray currents from high voltage electric lines find their way to a pipe line or other steel structure. On the other hand the currents employed were much stronger than would be set up in a pipe line by galvanic action, and so did not reproduce the actual conditions of service, but they enabled corrosion to take place in natural water and weak dissociated solutions under conditions similar to those that would be found in the pipe line carrying sewage. It was thought that this test would also show the manner of corrosion, as distinguished from the total amount of corrosion, better than the acid tests, and inasmuch as the real question at issue was one of pitting, and not one of general rusting, the electrolysis test seemed to be a more reliable one for the case at hand.

The results of the application of this test to various samples of steel showed clearly that mill scale has a marked influence on the uniformity of corrosion and the formation of pits. This suggested possible differences in the electrical condition of the mill scale on the different samples of steel submitted to us, and an investigation of this feature was also undertaken.

Description of Steel Samples

The following notes show the nature of the samples used in the experiments:

A. Steel received from Emil Kuichling, furnished by the Allegheny Steel Company.

11 pieces 6″ x 2″ x ⅜″

Surface covered with black scale.

Analysis (by Dr. J. C. Olsen)	Carbon	0.16%
	Manganese	0.31%
	Silica	0.03%
	Copper	0.002%

B. Ingot iron received from Emil Kuichling, furnished by the Allegheny Steel Company.

11 pieces 6″ x 2″ x ⅜″

Surface covered with scale, which is almost black, but slightly brown.

Analysis (by Dr. J. C. Olsen)	Carbon	0.02%
	Manganese	0.01%
	Silica	0.02%
	Copper	trace

C. Wrought iron received from Emil Kuichling, furnished by the Allegheny Steel Company.

11 pieces 6″ x 2″ x ⅜″

Surface covered with black scale, on which there was a slight film of yellowish brown iron rust, which could be easily rubbed off.

Analysis (by Dr. J. C. Oslen)	Carbon	0.07%
	Manganese	0.19%
	Silica	0.04%
	Copper	0.001%

D. Charcoal Iron Boiler Tubes received from Allegheny Steel Company.

3 pieces 6″ long cut in half lengthwise from 2″ tubes. These pieces were covered with a rather thick black scale, somewhat heavier at some points than at others. The surface presented the fibrous, stringy appearance common to wrought iron.

E. Steel Boiler Tubes received from Allegheny Steel Company.

3 pieces 6″ long, cut in half lengthwise from 2″ tubes. The scale was black and fairly uniform in distribution and thickness.

F. American Ingot Iron Boiler Tubes received from the Allegheny Steel Company.

3 pieces 6″ long cut in half lengthwise from 2-inch tubes. The scale on these pieces was black with a small amount of red oxide on the surface, not as much, however, as the American Ingot iron usually has.

G. American Ingot Iron Sheets received from the Allegheny Steel Company.

12 pieces 2″ x 8″ x $\frac{1}{8}$″

These pieces presented a dark surface covered with scratches, which probably resulted from the removal of most of the scale by a wire brush. The general character of the surface was smooth.

H. American Ingot Iron Plates received from the Allegheny Steel Company.

12 pieces 2″ x 8″. Gauge 10.2.

The surface of these samples was covered with a scale containing a large proportion of red oxide, giving them the appearance of rusted pieces. The scale was not very thick but uniform in distribution. The red oxide easily rubbed off on the hands.

I. Hot Rolled Steel Plate received from shop in Pierce Hall, Harvard University.

6 pieces 2″ x 8″ x $\frac{3}{16}$″
This steel had a black, tightly adhering scale of varying thickness often occurring in layers or 'scales.'

J. Carbon Steel Plate from Carnegie Steel Co.

12 pieces 2 ½″ x 8″ x ¼″
Heat number, 13,121.

Analysis,		
	Copper	0.0%
	Carbon	0.10%
	Phosphorus	0.011%
	Sulphur	0.024%
	Manganese	0.38%

These samples, as well as those listed under K and L, were stamped with the heat number. The scale around the edges was irregular in distribution, owing to abrasion during shearing. It was black, rather glossy in appearance, and fairly smooth and regular in the surface presented, except at the edges as mentioned above.

K. Copper Steel Plate received from Carnegie Steel Company.

12 pieces 2 ½″ x 8″ x ¼″
Heat number, 23,583.

Analysis,		
	Copper	0.23%
	Carbon	0.07%
	Phosphorus	0.011%
	Sulphur	0.028%
	Manganese	0.38%

L. Copper Steel Plate from Carnegie Steel Company.

12 pieces 2 ½″ x 8″ x ¼″
Heat number, 23,778.

Analysis,		
	Copper	0.53%
	Carbon	0.11%
	Phosphorus	0.10%
	Sulphur	0.025%
	Manganese	0.43%

Immersion Tests

In the first experiment strips of steel (A), ingot iron (B) and wrought iron (C) as received, were put in separate beakers containing distilled water and allowed to stand at room temperature (70° F.). The distilled water contained 3.5 parts per million of CO_2 and was saturated with oxygen. After 24 hours the water in the beaker that contained the ingot iron had less color than the other two and anlaysis showed that it contained less iron.

	Steel A	Ingot iron B	Wrought iron C
Area of metal wetted, sq. cm.	23	22	22
Quantity of water, cc.	370	375	395
Iron in water, mg. per litre.......	45	14	36

Samples of steel (A), ingot iron (B) and wrought iron (C) were next placed in beakers containing distilled water and tap water, and allowed to stand for various periods of time during which the appearance of the plates was noted and analyses of the water made to determine the amount of iron present in the ferrous and ferric condition. Variations in the conditions were secured by using hot and cold water and by comparing strips of steel from which the mill scale had been removed with similar strips with the mill scale left on except at the edges. Detailed records of these experiments were kept, but the results do not warrant publication, as they were so erratic that it was evident that all of the necessary conditions of the experiment had not been properly controlled. Suffice it to say that all three metals rusted badly in all of the experiments, and that such differences as were noted between the different metals were due more to experimental errors than to the character of the metals themselves. Generally speaking, the rusting was slightly greater in the case of the metals from which the mill scale had been removed, than in these cases of the metals on which the scale had been left, but in this comparison the differences were somewhat less with the wrought iron than with the steel or ingot iron. At the start, the mill scale on the steels appeared to exert a slight protective action, but after a few days this disappeared. On the whole the ingot iron showed somewhat smaller losses of iron than the other metals, but this was not true in all of the experiments, and the differences were never large.

After immersing samples of the three metals in weak N–50 sulphuric acid, N–50 acetic acid and a 10% solution of bleaching powder and obtaining heavy corrosion in all cases, the plates were examined under the microscope to see if any differences in the scale could be detected. The appearance of the scale of the American Ingot Iron was not greatly altered by the immersion, although a large amount of it had disappeared, exposing the metal beneath. The steel plates showed less loss of scale, but under the microscope the scale surface exhibited minute cracks and fissures, and in places small holes, through which the iron beneath had passed in solution, as evidenced by the deposit of red oxide close to these openings. These openings in the scale were much more numerous after immersion than before. The appearance of the wrought iron scale was not materially changed by immersion, but such loss of scale as occurred was uniform over the surface of the test piece.

Electrolysis Test

When two plates of iron are immersed in water and connected with a battery in circuit, a current of electricity will pass through the water from one plate (the anode) to the other (the cathode), and iron will be dissolved from the anode; in other words, the anode will corrode. If the plate forming the anode is uniform in composition, the corrosion will be uniform over its surface, and the loss in weight will be proportional to the current density. If the anode is not homogeneous in character, the density of the current will not be uniform over the plate, and the corrosion will be greater at some spots than at others. Thus no corrosion at all will occur over areas where some such insulating material as coal tar has been spread, but will occur in greatest degree where the raw metal is exposed.

The mill scale that is formed upon the surface in the manufacture of steel differs in chemical composition from the metal beneath it, being composed largely of iron oxides, together with some slag, and it is to be expected that its electrical resistance would be different. Moreover, the mill scale commonly occurs, not as a sheet of uniform composition and thickness, but as a series of flakes or scales, (hence its name) sometimes overlapping and varying greatly in thickness. This is often evident to the eye, but may be better observed by the use of a lens. Hence, when a sheet of steel covered with mill scale is used as the anode, it might be naturally expected that the current density would vary and that the corrosion of the metal would occur, not uniformly, but in spots. Conversely, if the corrosion produced by passing a current of electricity between electrodes is irregular, it may be inferred that the scale is not homogeneous in thickness or quality; and, further, that if different plates act differently when submitted to such a test, the inequality of the character of the scale will be measured by the irregularity of corrosion. These ideas were well illustrated by a series of experiments performed as follows:

Two plates each of steel (A), ingot iron (B) and wrought iron (C) were arranged in pairs in separate jars of water, parallel to each other and three inches apart, and connected in parallel with an Edison-Lelande battery, the current of which was found to be 0.88 volt. Each jar contained 2100 cc. of Brooklyn tap water (Hardness 37.5; alkalinity, 15.5; chlorine 12.0; carbonic acid, 5.0 parts per million). The plates were thickly coated with paraffin except that exposed surfaces, 3 inches long and one inch wide, were left facing each other in each pair of plates. At first no change occurred, but after one hour the ingot iron appeared to be rusting in spots and the wrought iron in streaks, the steel showing no sign of corrosion. After 1.5 hours, and again after 21 hours, samples of the water were withdrawn from each jar and analyzed for iron with the following results:

	Increase in Iron in Parts per Mil.	
	After 1.5 hours	After 21 hours
Water in jar containing the steel	0.3	2.9
" " " " " ingot iron	1.2	3.3
" " " " " wrought iron	1.5	6.1

After 24 hours the physical differences between the three plates were conspicuous; the wrought iron was rusting in streaks that nearly covered the entire surface, while the steel and ingot irons were rusting in spots, one particular spot on the steel being especially noticeable.

In order to hasten the action, a stronger direct current from a lighting circuit was then applied (55 volts and 0.2 ampere) and tap water allowed to flow freely through the jars, being directed against the exposed areas, in order to prevent the accumulation of gas at the anode plate. After three days the plates were examined. All were covered with rust, but when this was removed it was found that the wrought iron had corroded uniformly without pitting, but that both the steel and the ingot iron were badly pitted, the steel being the worst.

A second series of tests was then made using other plates of the same lots of steel, ingot iron and wrought iron, but with the mill scale removed in each case by grinding on an emery wheel. Submitted to a current of the same strength and for the same length of time, these plates corroded uniformly and without any sign of pitting. The wrought iron plate appeared to be slightly grooved, the steel plate showed a slight tendency towards a honeycombed structure, while the ingot iron plate was smoothly etched and had a bright silvery surface.

In order to corroborate these results the experiments were repeated using other pieces of metal, both with and without the scale, using a lighting current of 112 to 120 volts, and 0.12 to 0.18 amperes for four days; also with the current reduced to 2 volts and 2 milli-amperes for 22 days. In this case the samples used were A, C, E, G, H, I, J, K, L. The results were the same as those first obtained, namely, the test pieces from which the scale had been removed did not pit but rusted evenly. The wrought iron with the scale on did not pit, but corroded in grooves, the metal showing in general a uniform fibrous surface. The steel samples with the scale on and the ingot iron samples pitted, the pitting in the steel samples being invariably the deeper.

In certain of the plates holes were then drilled through the scale at regular intervals and the experiment repeated, thinking that corrosion might take place exclusively at these points. This was not found to be the case. Pits did occur at these points, but they also occurred at other points, indicating invisible fractures or openings in the scale. The number and depth of the pits differed in different samples of steel and ingot iron.

The loss of weight by rusting in these experiments did not differ greatly with the different materials, but comparing the slight differences the loss was greatest in the case of the wrought iron and least in the steel, as illustrated by the following figures, which show the loss in weight of different plates exposed for 22 days to a direct current of 2 volts and 2.0 to 2.8 milli-amperes.

Sample	Volts	Current Milli-amperes	Loss in weight grams per square centimeter
A Steel	2	2.8	.013
B Am. ingot iron	2	2.0	.015
C Wrought iron	2	2.0	.017

The electrolysis test therefore serves to indicate the *manner* in which plates corrode rather than the *amount* of the corrosion. Inasmuch as it is the pitting with which the water works engineer is chiefly concerned, this form of accelerated test appears to have some advantage over immersion tests in which strong corrosive acids are used. In these strong acids the action is essentially a chemical one, but in the dilute solutions used with the electrolytic test, the strict chemical action is subordinated to the electrolytic form of corrosion. This test, therefore, more nearly approaches the conditions of natural corrosion in water.

It has frequently been observed that with the ordinary acid tests the purer forms of metal show the smaller losses. This is a strict chemical action in which the mill scale, as well as the iron, is dissolved away. With the electrolysis test, however, the purity of the metal itself exerts less influence, and the scale remains for a longer period of time to become an important factor, as it does in actual service. Mention has been previously made of the fact that mill scale may exhibit marked differences of potential toward iron, due largely to its varying composition and thickness, which influence the resistance offered to the passage of an electrical current.

Galvanic Survey of the Mill Scale

According to the electrolytic theory of corrosion the solution of the iron is brought about by the action of currents that are set up between different particles of the metal that have different electrical potentials, as for example, between the pure metallic iron and various impurities such as carbon, manganese, slag, etc. This has been illustrated by Walker, Cushman and others by the use of the ferroxyl indicator. Purity and homogeneity, therefore, tend to diminish corrosion. It is believed that pits in steel occur at points where for some reason or other there are particles that have greater differences of potential from that of the metallic iron or the mill scale than are found elsewhere on the sheet. Possibly this may result from segregation of the impurities during the cooling of the ingot; possibly it is due to the effect of rolling, cooling and other treatment the mill scale undergoes. It is known, at any rate, that differences of potential exist between iron and its oxides, and it seems reasonable to believe that this is a very important cause of pitting, perhaps the most important factor of all.

It seemed to us, therefore, that a study of the potential differences between the mill scale at different points and the raw metal beneath might throw light on the relative liability to pitting of the various metals submitted to us for study. On account of the difficulty of making the necessary measurements with the samples immersed in water, the simple method was adopted of connecting the raw metal of a sample with its mill scale by means of wires, and placing a very sensitive galvanometer in the circuit, the two contact poles being the rounded ends of #18 copper wire. The galvanometer used was sensitive to less than one ten-millionth of an ampere. It was found that when both poles were put in contact with raw metal, no current could be detected, but that when one pole touched the raw metal and the other pole touched the scale on a piece of steel plate, a noticeable current was set up, which in some cases amounted to nearly one-millionth of an ampere. Usually the current in the galvanometer circuit was from the scale to the metal, and in the sample from the metal to the scale, that is, in the direction which would tend to make the iron dissolve. Occasionally, however, the current was in the other direction. On the steel plates the currents sometimes differed greatly at points only one millimeter apart; more often, however, there were areas where the current was relatively high and others where it was relatively low. Very slight currents were found in the case of wrought iron and cast iron indicating a great homogeneity of the scale, or less difference of potential between it and the metal.

Studying the mill scale of a steel plate with the microscope and comparing the observations with the current readings, it was evident that to a considerable extent the current varied with the thickness of the scale, but occasionally decided differences of current were found between points on the scale that looked exactly alike. It was noticed that when one pole was touched to raw metal, and the other to red rust (Fe_2O_3) little or no current was produced; and the greatest currents were set up between the raw metal and the black scale (Magnetic oxide), the brown scale on ingot iron giving results intermediate between the other two.

In order to compare the different samples submitted to us, areas of one square centimeter were marked out in squares, and what may be called a galvanic survey made, nine spots being tested in each square as shown in Figures 1 and 2. As a rule, about 200 galvanometer observations were made for each plate tested. The results were then tabulated and the percentage of

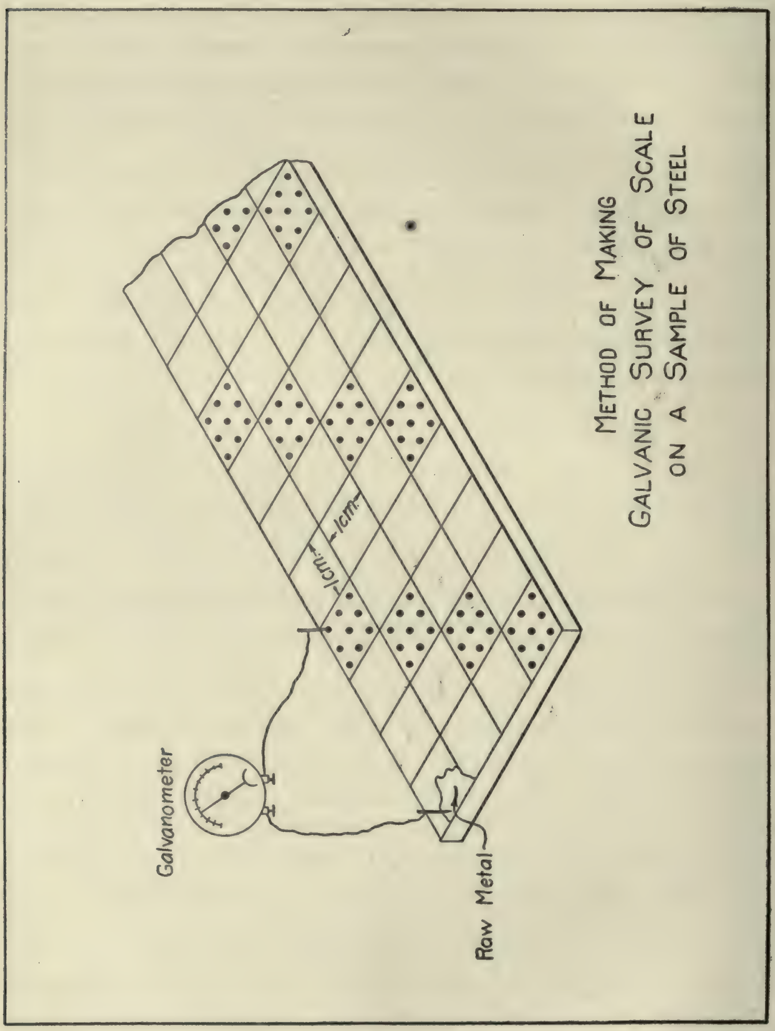
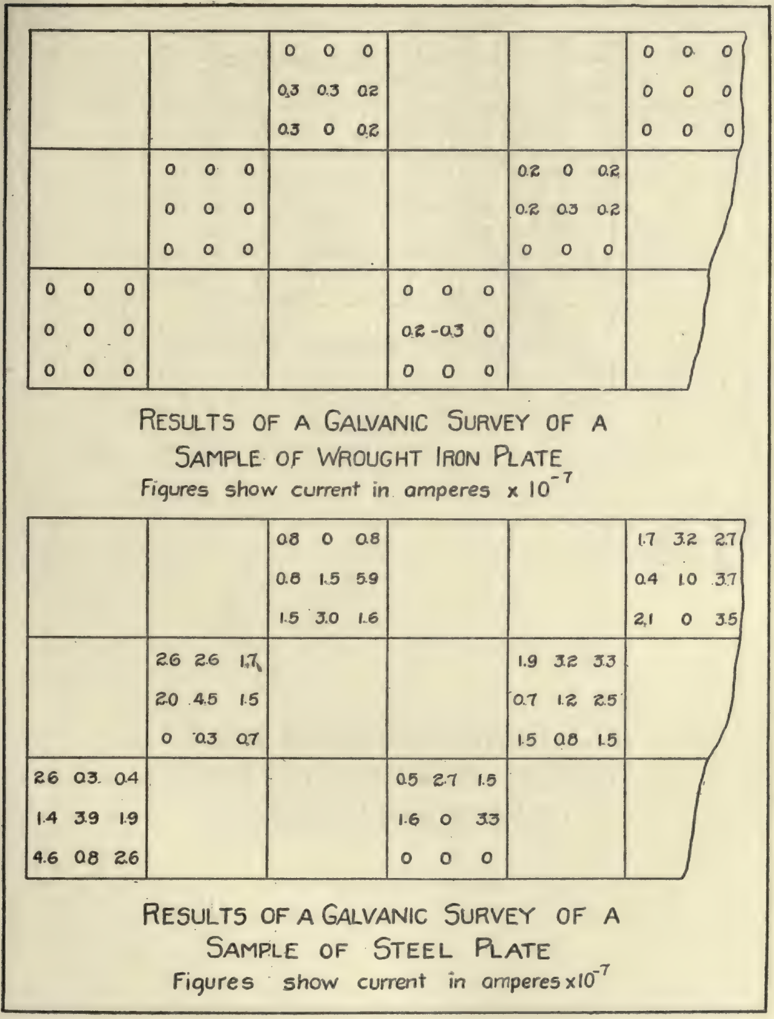

METHOD OF MAKING
GALVANIC SURVEY OF SCALE
ON A SAMPLE OF STEEL
1cm
1cm
Galvanometer
Raw Metal

Fig. 1



						0	0	0							0	0	0
						0.3	0.3	0.2							0	0	0
						0.3	0	0.2							0	0	0
			0	0	0							0.2	0	0.2			
			0	0	0							0.2	0.3	0.2			
			0	0	0							0	0	0			
0	0	0							0	0	0						
0	0	0							0.2	-0.3	0						
0	0	0							0	0	0						

RESULTS OF A GALVANIC SURVEY OF A
SAMPLE OF WROUGHT IRON PLATE
Figures show current in amperes x 10^{-7}

						0.8	0	0.8							1.7	3.2	2.7
						0.8	1.5	5.9							0.4	1.0	3.7
						1.5	3.0	1.6							2.1	0	3.5
			2.6	2.6	1.7							1.9	3.2	3.3			
			2.0	4.5	1.5							0.7	1.2	2.5			
			0	0.3	0.7							1.5	0.8	1.5			
2.6	0.3	0.4							0.5	2.7	1.5						
1.4	3.9	1.9							1.6	0	3.3						
4.6	0.8	2.6							0	0	0						

RESULTS OF A GALVANIC SURVEY OF A
SAMPLE OF STEEL PLATE
Figures show current in amperes x10^{-7}

Fig. 2

Fig. 3.

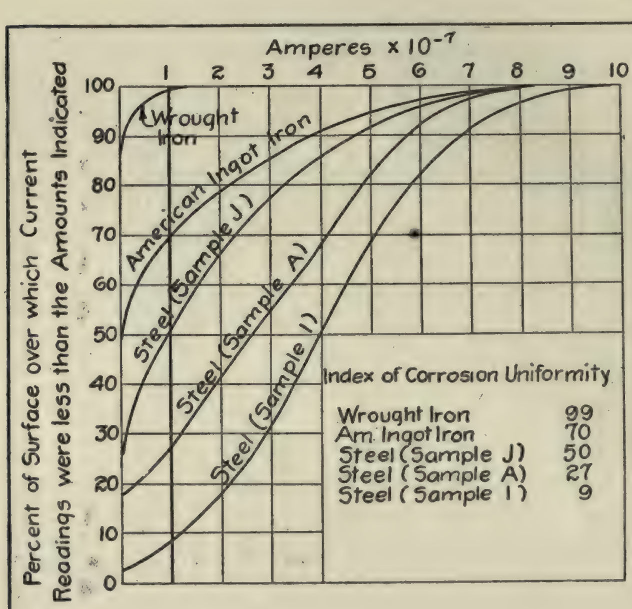


DIAGRAM SHOWING THE METHOD OF FINDING THE INDEX OF CORROSION UNIFORMITY

Fig. 4

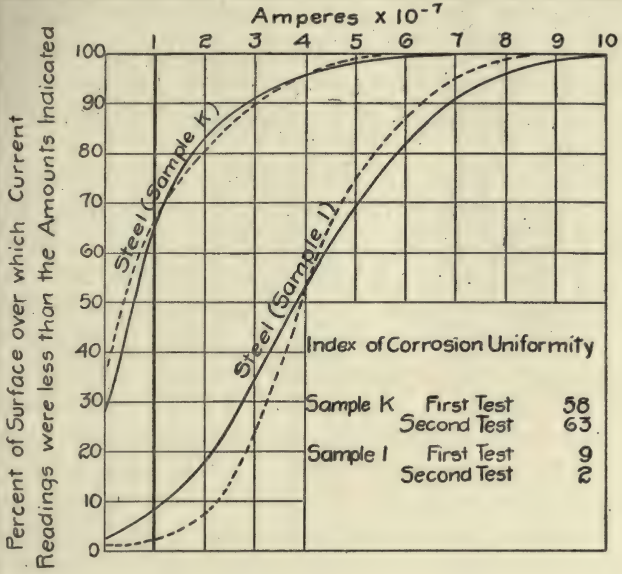


DIAGRAM SHOWING RESULTS
OF DUPLICATE GALVANIC SURVEYS
OF TWO SAMPLES OF STEEL

observations found for currents of different strength. It was assumed that this presented the percentages of the areas of the scale where currents of these strengths were likely to be set up. With the plate immersed in water, the actual strength of the currents would be different from those observed, and probably greater. The results, therefore, must be considered as having a relative value only.

In order to better compare the different plates, the percentages of area, where the current found was less than certain strengths, were then added together serially, and these figures were tabulated and plotted with the strength of current as abscissae and the percentage of areas as ordinates. Typical curves, based on the average of several surveys in each case, are shown in Figure 3 for wrought iron, ingot iron, ordinary mild steel and a steel which was found to pit badly. It will be seen that the differences between these curves are very striking, the wrought iron showing a much lower and more uniform current than the ingot iron or steel. In making this summation the points where the current was found to flow from the scale to the raw metal were included with the points where there was no current, as it was assumed that at these points no solution of the iron would occur.

Index of Corrosion Uniformity

If the uniformity of corrosion over the surface of a scale covered plate varies with the uniformity of the current set up between the scale and the metal at different points, a figure representing this uniformity of current may be considered as a sort of index of corrosion uniformity. If the current is the same at all points or if no current is shown by the galvanometer between the raw metal and all points on the surface, the index may be taken as 100. This is the case of plates from which the scale has been removed. If practically no current is found over 75% of the area, the index of uniformity may be taken as 75, and so on. The difference between 100 and this figure is therefore an index of the liability to irregular corrosion, or pitting.

As the galvanometer readings were not accurate below one ten-millionth of an ampere, with the instrument read, and as very minute currents are of less effect than stronger currents, the percentage where no current was found did not appear as fair a criterion for estimating this index as the percentage where the current was less than one ten-millionth of an ampere (A x 10^{-7}). In other words, a current of this magnitude was considered as practically negligible. For the purposes of this comparison, therefore, the index of corrosion uniformity was taken as the percentage of the surface area of the plates over which the galvanic current was found to be less than one ten-millionth of an ampere, while the index of pitting was taken to be 100 less this percentage. These values are purely arbitrary but serve to provide a basis for a comparison of the tendency of different samples to pit. Illustrations of these values are given in Fig. 3, where the curves show the index of corrosion uniformity and its index of pitting to be as follows:

	Index of Uniformity	Index of Pitting
Wrought iron	99	1
American Ingot iron	70	30
Steel	50	50
Pierce Hall steel	9	91

The current values from which these curves were plotted represent the average of several samples.

In order to determine the accuracy of this method of making readings and computing the index of corrosion uniformity, duplicate tests were made upon certain samples several weeks after the first ones, with the following results:

	Index of Uniformity		Index of Pitting	
	1st Test	2nd Test	1st Test	2nd Test
Wrought Iron (A)	99	100	1	0
Steel (K)	66	64	34	36
Steel (L)	58	60	42	40
Steel (I)	9	2	91	98

Fig. 4 shows the curves obtained for two samples of steel that differed considerably. It will be seen that they correspond quite closely at the point which has been chosen to determine the index of corrosion uniformity.

Thinking that the amount of moisture and occluded gases within the pores of the scale, or between the scale and the metal, might influence the galvanic currents flowing, samples were dried for two hours at 100° C., and then subjected to readings with the galvanometer. These tests did indeed show less current flowing between the scale and metal after moisture had been driven off, and the index of corrosion uniformity was consequently raised somewhat by drying the sample. In the case of wrought iron the index was increased from 99 to 100; in the case of steel, from 58 to 72. (See Table) Results obtained after soaking samples in water and drying did not differ materially from those made with samples under ordinary atmospheric conditions. The reduction of moisture content obtained in the drying experiments represented a greater percentage variation than any which would occur in ordinary atmosphere. Accordingly it was considered satisfactory to compute the index of uniformity for a given sample from tests made under ordinary atmospheric conditions.

Relation between Pitting of Plates and the Index of Corrosion Uniformity

In order to see whether there was any relation between the index of corrosion uniformity and the actual pitting as induced by the electrolysis test, a piece of metal that had been carefully surveyed and found to have a low index of uniformity, i.e., a high index of pitting, was placed in a beaker of tap water and connected as the anode with a similar plate, while a 116 volt direct current was sent through the battery. On observing the plate closely with a lens, it was seen that rusting began first at the points where the current had been found below the average for the plate; and the irregularity of the formation of iron oxide was marked. A plate that had a high index rusted more uniformly.

PER CENT OF SURFACE AREA OVER WHICH THE OBSERVED GALVANIC CURRENT WAS LESS THAN THE FIGURES INDICATED

Amperes x 10^{-7}

Sample	0	1	2	3	4	5	6	7	8
					Wrought Iron				
A1.......	81	99	100						
A2.......	70	98	100						
					American Ingot Iron				
B........	54	72	80	88	94	98	99	100	100
H1.......	36	55	68	78	86	91	96	98	100
H2.......	55	82	88	92	95	97	98	98	100
					Steel				
C	17	27	42	55	68	82	92	97	100
1	3	9	18	34	53	67	82	91	97
I Duplicate	2	2	9	24	56	74	87	96	99
J	26	50	68	84	91	94	97	100	100
K	36	67	80	90	96	99	100	100	100
K Duplicate	29	63	84	95	97	98	99	100	100
L	18	58	71	81	87	91	95	98	100
L Duplicate	11	62	82	[illegible]	98	99	100	100	100
L dried at 100°C.	15	72	93	99	100	100	100	100	100

The appearance of plates representing the three metals tested, namely, wrought iron, ingot iron and steel, has already been described under the electrolysis test. The tendency to uniform corrosion varied with the index of uniformity, the plates which gave an index of 98 or 99 being practically free of pits, while the plates which had an index of 50 to 75 showed marked pitting. Other evidence of the general nature of the action over the surface of plates with high index of uniformity was provided by the general disappearance of scale. This was in marked contrast to the deeply pitted plates, where the bright metallic surface was exposed only for a short distance around the centres of pitting. The following figures show the relation between the index of corrosion uniformity, and the number and depth of the pits that developed under the electrolysis tests under comparable conditions:

Sample	Index of corrosion uniformity	Index of pitting	Number of pits per sq. inch	Depth of pits in m.m.		
				Max.	Min.	Avg.
Wrought iron	98	2	3.6[1]	0.6	1.4	1.0
American Ingot Iron	70	30	6.8	1.6	3.2	2.1
Steel.............	50	50	10.0	1.3	3.5	2.2

When corrosion occurs in plates immersed in water through the differences of potential between scale and metal, it would appear necessary to have the water come in contact with both the scale and the metal in order to furnish the necessary electrollyte, and supply oxygen for the oxidation of the iron. This introduces another factor, namely, the porosity of the scale. To some extent this porosity is probably taken into account by the galvanometer test. Microscopical examination of the scales showed, in many instances, the presence of minute cracks through which water might enter and come in contact with the metal. In general, these cracks were more numerous in those samples that showed a low index of corrosion uniformity. In some of the steels the appearance of the scale resembled a clayey soil after being sun dried. That is, it was covered with hair cracks. In others, the scale had the appearance of microscopic beds of lava.

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[1] These were grooves rather than pits.

On the whole it may be said that the index of corrosion uniformity as determined by the galvanic survey of the scale, appears to give a fair measure of the probable liability of the surface of the metal to corrode in an irregular manner, that is, to pit.

EXPERIMENTS WITH COPPER STEELS

That manganese, sulphur and some other impurities likely to be found in steel stimulate its corrosion is the conclusion of a number of observers. This is particularly true if these impurities are irregularly distributed throughout the mass of the metal. It is unnecessary to review the theoretical reasons advanced for this belief further than to say that they are based on the electrolytic theory of corrosion, and deal with the changes in conductivity and resistance produced within the metal by these impurities. It has been claimed that some other metallic elements when present in small quantities, have an opposite effect upon corrosion; that is, that they retard action. Chief among these is copper. Campbell[1] says that copper occurs as an impurity in many steels, particularly that made by the Bessemer process, and may be present to the extent of 0.3 to 0.5 per cent.

Opinion seems to be divided in regard to the effect of copper in retarding corrosion. There is evidence to show that it materially decreases the solubility of steel in sulphuric acid, but the question arises as to its effect upon the electrical properties of the steel. Sang[2] states that the depolarizing effect of the electronegative metals, such as copper and lead, might be expected to hasten the rusting of iron or steel. If copper protects, and if steel ordinarily contains as much copper as Campbell has stated, then it is rather surprising that the copper steels have not given better service.

The samples tested, (J, K and L) contained 0, 0.23% and 0.53% of copper respectively. The use of copper steel having been suggested for the Rochester sewer outlet pipe, some experiments were undertaken to determine its advantages, if any, for this service. These included immersion tests, electrolysis tests and galvanic surveys.

[1] Metallurgy of Iron and Steel, p. 358.

[2] Sang, Corrosion of Steel, p. 37.

Immersion Tests with Copper Steels

Strips of the metal, 2½″ x 8″ were buffed and cleaned of dirt and grease, weighed and placed in glass trays, supported upon four ⅛″ pieces of the same metal. 450 cc. of 25% sulphuric acid, enough to completely immerse the strips, was then poured into the tray. Twice during a period of 24 hours this acid was renewed and the solution was stirred occasionally. At the end of 24 hours, the plates were removed, washed, dried and weighed. In the case of sample J, which contained no copper, the action had been violent, as evidenced by the evolution of hydrogen and the bright etched surface of the plate. Sample L, which contained the most copper showed the least action, as far as surface appearance indicated. The following losses in weight were obtained. The loss in weight is seen to be much greater in the steel that contained no copper than in the other two.

IMMERSION TEST WITH 25% SULPHURIC ACID

Sample	Per cent of copper	Loss in weight in grams	Area exposed in Sq. Cm.	Loss of weight in grams per Sq. Cm.
J................	0	27.0	307	.0880
K................	0.23	5.4	270	.0200
L................	0.53	5.1	258	.0198

The effect of a dilute sulphuric acid solution was also tried. For this purpose an N–50 solution of acid, (i.e. about 0.1%) was used, the cleaned plates being placed in two-quart glass jars and covered with the acid. After 26 days the following losses of weight were found:

IMMERSION TEST WITH $\frac{77}{50}$ SULPHURIC ACID

Sample	Per cent of Copper	Weight in Grams	Area exposed in Sq. Cm.	Loss in grams per Sq. Cm.
J................	0	3.00	234	.0128
K................	0.23	2.90	247	.0117
L................	0.53	3.15	231	.0136

These results were in marked contrast to those in which the stronger acid was used, as they showed only slight differences between the losses from metals containing different amounts of copper.

Immersion tests were also made using sodium chloride solutions of two strengths, namely, 0.3% and 3%, the latter having a salinity about equal to that of sea water. The losses in weight after 26 days were as follows:

IMMERSION TESTS WITH SALT SOLUTIONS

Sample	Per cent of Copper	Loss of Weight in grams per sq. cm.	
		3% solution	0.3% solution
J................	0	.0015	.0013
K................	0.23	.0015	.0019
L................	0.53	.0019	.0021

The general results of the immersion tests go to show that where the action is emphatically a chemical one, as in the case of the strong acid test, the presence of copper tends to reduce the action; but where, as in the tests with weak dissociated acids and salt, the electrolytic form of corrosion predominates, copper does not reduce corrosion, but on the other hand, tends slightly to stimulate it.

Electrolysis Tests of Copper Steels.

Electrolysis tests of the copper steels were made, according to the method previously described. A lighting circuit was the source of current, and the plates were arranged in separate jars in the form of batteries connected in parallel with the anode and cathode separated by a distance of three inches. A low current of 2 volts and about 2 milli-amperes was first used, a resistance coil being employed for the reduction of the current. This test extended over a period of 22 days, during which running tap water passed constantly through the jars containing the plates. The following losses in weight were recorded:

ELECTROLYSIS EXPERIMENT WITH LOW CURRENT FOR 22 DAYS

Sample	Per cent Copper	Voltage	Current in Milli-Amperes		Loss of weight in grams per sq. cm.
			At start	At finish	
J #13,121	0	2	2.5	2.5	.0072
K #23,583	0.23	2	3.2	2.9	.0082
L #23,778	0.53	2	3.2	3.0	.0080

Sample J, which had no copper, was found, upon inspection after the test, to have developed pits of considerable depth at various places on the surface. Except around these pits the scale remained intact. Samples K and L showed a somewhat larger area of general corrosion and most of the pits were not as deep as in the case of J. Less of the original scale remained on these plates.

Another test was made with these steels using a 112-volt current. This experiment extended over a period of 51 hours. Readings at the start showing a current strength of .23 to .25 amperes, and at the close .17 to .18 amperes. An examination of these plates showed that all of them had been subjected to irregular action with the formation of pits. Samples J and K presented much the same appearance, patches of black scale adhering to the plate in patches where the action had not exposed the bright metallic surface. The latter was rough and irregular in contour, the result of uneven loss of metal. The exposed metal of Sample L, which contained the most copper, had a dull lustre owing to a larger number of small pinhole pits. Some of these extended quite as far into the metal as did the larger pits on J and K, and gave to the plate a honey combed appearance.

Galvanic Survey of Copper Steels

The index of corrosion uniformity for samples J, K and L varied between 51 and 67; that is, they did not cover a very wide range. Sample J, with 0% copper, had the lowest index, namely 51, and consequently the highest index of pitting; and so far as observed, the electrolysis tests showed that this steel possessed a slightly greater tendency to localized action than the others, particularly under the influence of a low current for a long period of time. The differences, however, were not marked.

Conclusion as to Copper Steels

From the tests made it was concluded that the presence of small amounts of copper in steel, while they may retard corrosion by strong acids, do not serve to protect the steel against corrosion in weak acid solutions or in ordinary water. The presence of copper does not materially alter the electrical conditions of the scale, and does not, therefore, protect the metal against pitting.

Conclusion as to Ingot Iron

The samples of American ingot iron plates tested were found to have an index of corrosion uniformity somewhat higher than that of ordinary steel plates, with or without copper, but lower than that of wrought iron. So far as failure by pitting is to be feared, therefore, the ingot iron may be regarded as somewhat better than steel, but probably not enough better to justify any great difference in cost. Exposed to severe acid corrosion, ingot iron is probably more serviceable than steel, but under ordinary conditions of corrosion in soil or water, it has only a slight advantage over steel.

Conclusion as to Wrought Iron and Steel

Wrought iron has a very much higher index of corrosion uniformity than steel or ingot iron and is much less likely to pit. This seems to be in accord with experience. Under conditions of severe chemical corrosion, sufficient to remove the mill scale and silicates, or under conditions of atmospheric corrosion, when the electrolytic form of corrosion does not predominate, there is probably little difference between the two metals.

Effect of Removing the Mill Scale

A partial removal of the mill scale tends to increase corrosion as it gives opportunity for electrolytic action between the scale and the raw metal. Scale becomes chipped off in handling and in fabrication.

The complete removal of the mill scale from steel plates increases its index of corrosion uniformity from about 50 to nearly 100 and this reduces materially the danger of pitting. The electrolysis tests made with steel plates, from which the mill scale was removed, did not show pitting in a single instance. Scale removal appears, therefore, to be a secure method of protection against pitting. To some extent it has been practised, the mill scale being removed by pickling in acid, by sand blasting, etc. These processes unfortunately are expensive, but may be justified under some conditions. Steel of ordinary quality with the mill scale removed will probably withstand pitting better than the more expensive ingot iron and copper steels, and just as well as wrought iron itself.

It is possible that some method may be found to modify the mill scale during manufacture so as to make it more uniform or improve its electrical condition, or make it more easily removable. It certainly seems as if the next step in advance in steel manufacture lies in securing a better control of the character of the mill scale. An extended study and series of experiments on the formation, composition and electrical properties of scales produced at different temperatures might determine the conditions that must be controlled to produce a satisfactory scale. If a satisfactory scale cannot be obtained the only apparent remedy for pitting is scale removal.

SUMMARY

It is the opinion of the authors that the experiments and observations outlined in the foregoing pages warrant the following general conclusions relative to short time tests for corrosion, and to the part played in corrosion by mill scale.

(1) Accelerated corrosion tests of iron and steel plates made by immersion in strong acid solutions are of little value as indicating the probable corrosion of the metals in water under conditions of actual service.

(2) Accelerated tests made in running water by the use of a current of electricity give results that indicate the *manner* in which the plates will probably corrode in service; that is, whether by pitting or by general corrosion.

(3) When steel pipe lines fail, they do so by the formation of numerous pits that ultimately form holes and cause leaks. An important factor in the formation of pits, commonly recognized but by no means fully appreciated, is the mill scale.

(4) Steel plates that pit badly under the electrolysis test when the scale is left on do not pit after the scale has been removed.

(5) A galvanic survey of the mill scale, made by determining the current that will pass through a sensitive galvanometer placed in the circuit of wires that connect the mill scale with the metal beneath, gives results that differ materially for wrought iron and steel, and from which an index of the uniformity of corrosion may be calculated that bears a general relation to the liability of the metals to form pits.

(6) The electrolysis tests and the galvanic survey show that wrought iron has a less tendency to pit than steel, and that American ingot iron is intermediate between the two, but resembles steel more nearly than it does wrought iron.

(7) Steels containing copper differ but slightly among themselves and from steel that contains no copper, in their tendency to form pits.

(8) To protect steel or ingot iron against failure by pitting, the best remedy is the removal of the mill scale. Efforts should be made to reduce the expense of doing this, or to modify the character of the scale during its manufacture. This appears to be the direction in which future improvements in the manufacture of steel plates for pipe-lines should lie.

ON RECENT PROGRESS IN THE ELECTROLYSIS OF ALKALINE SALTS

(*Wilderman Cell*)

By Dr. M. Wilderman, Ph.D., B.Sc., (Oxon)

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a. *Introduction*

In the following a short description of the Wilderman Cell shall be made and its essential features both technical and electrolytical, as distinguishing the same from all other mercury systems shall be given and explained on a scientific basis, so as to give a clear idea of the progress thus made in the electrolysis of alkaline salts both from the practical and theoretical point of view. It should be added that a large installation with the Wilderman Cell has been put up at the Zellstofffabrik Waldhof Mannheim Germany for a production of 10,000 tons of bleach per annum, which has been working very successfully from the first day till now without interruption for about 16 months, and that this installation is now being increased for a production of 14 to 15,000 tons of bleach per annum, so that the technical results given here are no longer of a problematic but of a thoroughly reliable character; some of the first cells have been working by now 19 months.

b. *Description of Cell, its mechanical and chemical strength and essential features*

In Table I. a sketch is given to illustrate the construction and working of the Wilderman Cell. The Wilderman Cell consists of a decomposing compartment (a) and of a combining compartment (b) which are separated by a partition composed of superimposed troughs containing a quantity of mercury which has free surfaces exposed in the combining and in the decomposing compartments. (G) shows the anodes. The inner compartment (a) contains a saturated solution of sodium chloride or potassium chloride, the outer compartment (b) contains caustic soda or caustic potash of about 20 to 22%. The current is passing from the anode (G) through the brine to the mercury in the troughs and from here back to the dynamo or to the next cell; alkaline metal is thus deposited by the current on the surface of the mercury and forms immediately therewith an amalgam, while the chlorine is separated on the anode (G) and is conducted away for the production of bleaching powder or chlorates, etc. Into the mercury of the troughs the teeth (T) of the stirrers (S) are dipping so as to effectually mix the amalgam formed on the top surface of the mercury with the mercury beneath it.

A special feature of the Wilderman Cell is that in every and in all its parts it is built of iron covered with ebonite of Dr. Wilderman's invention which stands both caustic and chlorine excellently. One millimetre of this ebonite stands about eight years chlorine and is by caustic not affected at all. Through this I was able to build a cell which combines the strength of iron as is requisite in the heavy chemical industry with the chemical strength and life of my ebonites and a cell was obtained which is capable to live 15 years and longer and which practically requires no repairs.

Another special feature in the construction of the Wilderman Cell is that the super-imposed troughs can be put ad libitum far from one another so that the surface of the anode is many times greater than that of the cathode. On this account the current density is very high upon the mercury surface, but comparatively small on the anode surface, so that graphite anodes instead of platinum electrodes can be used, and at the same time much greater current densities can be obtained with the same volts. This is not possible with the other cells where the anode is of necessity smaller but not larger than the cathode.

A third special feature of the Wilderman Cell is that the mercury is placed in the vertical wall and not at the bottom of the cell and that it is supplied with stirrers which always keep the mercury surface perfectly clean from dirt which is important for the efficiency and the good work of the cell. All the dirt from the brine as well as the decomposed carbon settles at the bottom and not on the mercury. Contrary to this, all the dirt and the decomposed carbon settle down in cells with horizontal mercury or horizontal diaphragm on the mercury or the diaphragm itself. The Wilderman Cell has also no diaphragms to replace so that there are no causes for interruption of its work. At the Zellstofffabrik Waldhof very cheap and inferior salt is used containing about 4% sulphates, calcium, magnesium, iron, slate, etc. and still the cell has to be cleaned only once in 6 to 8 months; with better salt it should work uninterruptedly for a year and longer.

c. *New principle of transportation of the amalgam from the decomposing to the combining compartment by buoyancy*

Instead of the amalgam remaining as in other mercury systems on the top surface of the mercury and leading here to the formation of strong eventually of solid amalgams, the top layer of the mercury amalgam is mixed up in the Wilderman Cell by the stirrers dipping into the mercury with the rest of the mercury on the chlorine side, so that the concentration of the amalgam on the top surface is made comparatively very dilute and the metallic sodium is uniformly distributed through the whole mass of the mercury on the chlorine side down to the lower rim of the trough (r). At the same time *the special shape of the troughs, their narrow dimensions and the whole position of the stirrers are such that when the amalgam is brought by the stirrers under the lower rim of the trough it is at the same time also below the mercury on the caustic soda side.* As the amalgam at the lower rim of the trough is lighter than the mercury on the top on the caustic side which is practically free from sodium, the amalgam rises on the caustic side immediately from below the rim to the surface of the mercury by *buoyancy.* From the top surface of the mercury on the caustic side the sodium or potassium are removed with enormous rapidity by the small carbons (d) which are in electrical contact with the amalgam, forming with it a local battery, so that the mercury on the top is practically free from sodium or potassium. On this account it may be taken as approximately correct that the speed with which the amalgam rises from below the rim of the trough to the top surface of the mercury is directly proportional to the concentration of the amalgam below the rim of the trough or on the chlorine side.

d. *The old method of bodily transportation of amalgam from the decomposing to the combining compartment leads to small current densities and makes the transportation artificial and limited to strict conditions of work*

In all other mercury cells the sodium entering the surface of the mercury remains in the top layer of the same, its thickness being perhaps only a small fraction of a millimetre, because the amalgam is lighter than mercury, while all the rest of the mercury below practically remains free from sodium. In all mercury cells there has to be provided a partition with a mercury seal between the decomposing and combining compartments in order that the liquids should not mix, and the bodily transportation of the amalgam always takes place through the mercury seal by some sort of mechanical means, be it by tilting of the whole vessel or by pumping or by syphoning, etc. During this transportation the poor amalgam from the lower layers of the mercury passes through the mercury seal first, while the rich amalgam from the top surface of the mercury remains to a great extent back in the decomposing compartment, because a part of the mercury amalgam must be left back to preserve the mercury seal and to prevent the mixing of the liquors. This gradually leads to the formation of very rich and solid amalgam which is then skimmed off at the mercury seal and leads to a diminution of efficiency of the cell. Because of this we have in all mercury cells, where the amalgam is bodily transported from the decomposing compartment into the combining and vice versa the following technical conditions and principles as unavoidable: the amalgams formed must remain dilute, mobile so as to be able to transport them more easily to the decomposing compartment and so as to avoid as far as possible the formation of solid amalgam. On this account all these processes can work only with comparatively small current densities. The practice has shown in case of good mercury cells such as Castner or Solvay, that the most suitable current densities are about 6 to 8 amperes per decimetre square of mercury and that as soon as higher current densities are tried they suffer from the formation of solid amalgams, eventually from explosions owing to the decomposition of the amalgam and the formation of hydrogen with the chlorine and such cells can also work only comparatively short periods without being stopped and cleaned (such a cell is known to me on the Continent).

e. *The new principle of transportation of amalgam by buoyancy leads to very high current densities; it also makes the transportation self-regulating and independent of strict conditions of work; it makes the formation of solid amalgam impossible*

Contrary to the above we do *not* transport the amalgam bodily from the chlorine side to the caustic side in the Wilderman Cell. The mercury on the caustic side is kept in the cell perfectly still and upon this depends to a very great extent the good efficiency of the cell and the purity of its products. The object of the stirrers is solely to make the amalgam on the chlorine side of a uniform concentration down to the lower rim of the trough so as to keep on the one end the amalgam on the surface thin and to make on the other end the transportation of the amalgam to the top of the mercury surface on the caustic side by buoyancy possible and effective. This enables us to work with quite enormous current densities unknown and inaccessible before. The higher the current density is which we employ the greater is the concentration of the amalgam on the chlorine side and below the rim, and the greater is the speed with which the amalgam is brought by buoyancy from below the rim to the top surface of the mercury and vice versa, this speed being as explained above directly proportional to the concentration of the amalgam below the rim or to the current density. The process of transportation is therefore here in itself self-regulating and automatical and does not require any adaptation of all conditions of work to the current density employed, does not require special regulation, supervision as we find it in all other mercury cells with bodily transportation of the amalgam; in fact the Cell cannot be upset in its normal work. At the Zellstofffabrik Waldhof Mannheim small cell units are used, which occupy only three metres square floor area, but the cells work already with 6,000 ampères each, while the current densities are still only 30 to 33 ampères per decimetre square of mercury. We are however able to work with current densities up to 60 to 70 ampères per decimetre square of mercury, almost up to the concentration of solid amalgam, without the least danger of formation of solid amalgam. Through such a cell very much more current can be sent if the electrical energy is cheap enough and if it pays to do so. The Wilderman cell is therefore to be characterised and designated in the first instance as the cell of very high current densities, the highest possible and imaginable for a mercury process, as the cell which is in all its parts of the process self-regulating and which cannot suffer from the formation of solid amalgam.

The following Table gives the current density per decimetre square of mercury in the Wilderman Cell at different volts at 70° C,

Volts.......	3.93	4.32	4.72	5.11	5.5	5.89	6.28	7.06	7.85
Current den.	10	15	20	25	30	35	40	50	60

Diagram 1 gives the volts and current densities in the Wilderman Cell and in other mercury and diaphragm dells. It is to be seen from the same: 1st, none of them are able to get the same current densities with the same volts; 2nd, none of them are able to work with the same current densities as the Wilderman Cell.—(P.T.O.)

f. *Which now are the important technical consequences of high current densities and of the self-regulating properties in the Wilderman Cell?*

(1). In the first instance we are able to work the power installation at its maximum capacity, that is most economically, the same cells taking up automatically all the energy the power installation is capable to supply at any given moment.

(2). The higher current density leads to *higher efficiency* and the *practically total absence of hypochlorides.*

When the current is passing from the anode to the cathode it decomposes the sodium chloride into metallic sodium and chlorine, the sodium entering into the mercury and the chlorine separating on the anode. This is the electrolytic process of decomposition. At the same time however the following two chemical reactions of recombination of the decomposed elements take place, and it is evident that upon the speed of these reactions depends how high the efficiency of a given mercury system can be.

The one reaction is: the sodium of the amalgam combines with water giving caustic soda and this with chlorine gives hypochlorides and chlorates which destroy the anodes. The second reaction is the direct recombination of chlorine with the sodium of the amalgam to sodium chloride. According to the laws of mass action in heterogeneous systems the speed of these two reactions will be the slower the smaller the surface of the mercury in contact with the liquid and the smaller the concentration of the sodium in the top layer of the amalgam. In the Wilderman Cell the concentration of the amalgam is made by the stirrers on the top surface very small, and as the current densities in the same are about five times as great as those of other good mercury cells, the surface of the mercury exposed to the liquid is for the same production also about five times smaller, and therefore the speed of the two chemical back reactions is correspondingly smaller. On this account the Wilderman Cell is and must be distinguished from all other mercury cells both by a much better efficiency and by very much smaller amount of hypochlorides.

The efficiency of the Wilderman Cell when specially attended to is 94%, the technical efficiency of the factory at the Zellstofffabrik Waldhof, owing to losses, is 90 to 92% for bleach and about 90% for caustic. The technical efficiency of Castner and Solvay is about 85%; of others is not well known to me. Diagram 2 gives the efficiency of different systems as given by the authors themselves at different concentrations of the caustic. It will be seen that no mercury and no diaphragm system is capable of getting the efficiency of the Wilderman Cell at the same concentration of the caustic, since in the diaphragm cells the efficiency drops very rapidly the higher the concentration of the caustic.

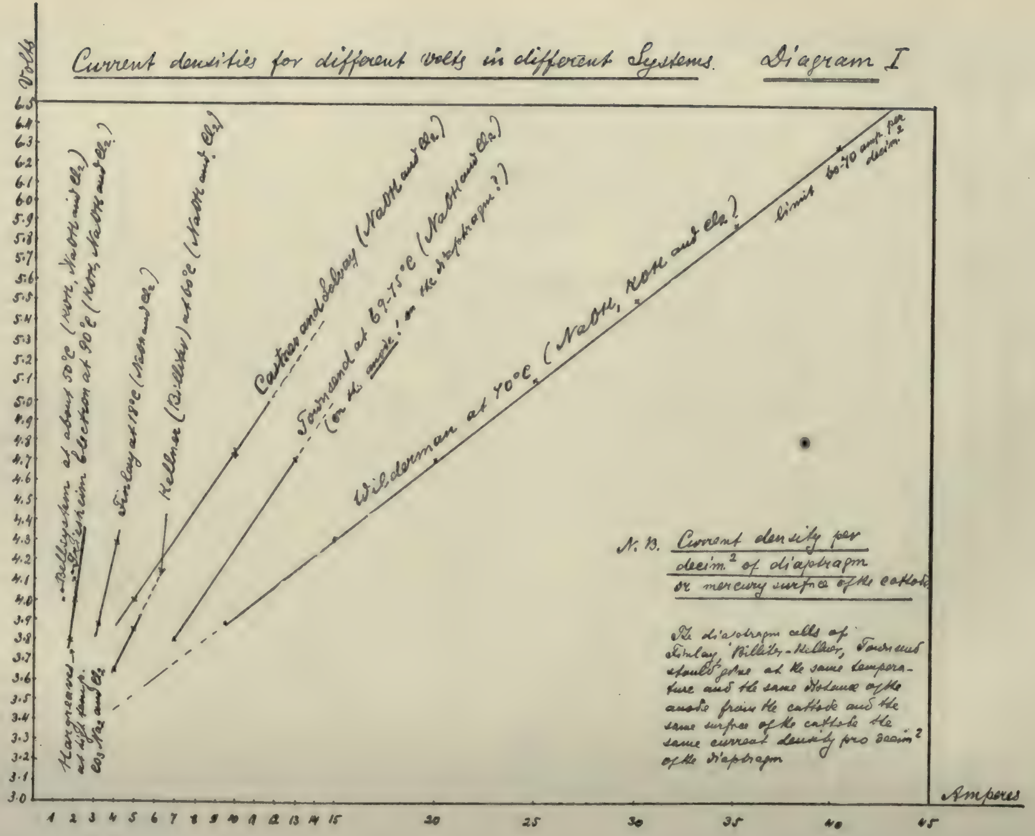
The amount of hypochlorides in the brine at the Zellstofffabrik Waldhof is only .02 to .04% and none in the caustic. As known all other systems suffer from hypochlorides in the brine and a great number of diaphragm systems have also hypochlorides in the caustic. The first destroy the anodes, the second are injurious to the evaporating installation and to the melting pots. The amount of graphite requisite per ton of bleach is therefore considerably smaller in the Wilderman Cell than in those suffering from hypochlorides and using graphite anodes.

(3). *High current densities lead to great economy in the cost of the installation and in the cost of production*

High current densities mean a small cell for a large production, one cell for many of them. At the Zellstofffabrik Waldhof a small cell of 3 square metres floor area works with 6,000 ampères; the whole production of 15,000 tons of bleach per annum requires only 80 cells. This means also that we require less land, less building, foundations, less electrical conductors, anodes, less mercury, circulation pipes, less labour, etc. The whole building of the cell room for 15,000 tons of bleach is about 15 metres by 60 metres; we use about 80 grammes of mercury per ampères, where some of the best mercury systems working with syphoning and pumping use 250; we require only 4 men per shift to attend all the cells for taking samples, for filling and emptying the same, and 1 man per shift to keep the cell-room clean; with the very bad salt we use we require for cleaning the cells 4 men per annum, counting together the whole time requisite for it; with better salt we should require correspondingly less; we used 2 men to attend the good contacts in the whole installation, as we found that it paid to do so, and we hope to be able to reduce this labour as well. The small number of cells and their long time of work also mean a great reduction in the losses of caustic and of mercury and makes also the artificial heating of the cells by steam unavoidable for cells with small current densities, quite unnecessary.

(4). *The Wilderman Cell as producer of caustic potash*

As the solubility of metallic potassium in mercury is much smaller than that of metallic sodium the mercury processes could hitherto work only with very small current densities when using potassium chloride, and they encounter great difficulties chiefly owing to the formation of solid amalgam to work for caustic potash on a technical scale. At present only two systems are working for caustic potash successfully; one is Greisheim electron which is working at Greisheim, Electrochemische Werke Bitterfeld, Westeregel, the other system is the Bell system working at Aussig, Austria, and at Salzbergwerk Neu-Stassfurd, Chemische Fabrik Buckau, etc. The current density of the first is 2 ampères of the second 1.5 ampères; the Wilderman Cell is capable of working with potassium chloride as with sodium chloride up to 60 to 70 ampères per decimetre square of the mercury. If it works with about 30 ampères per decimetre square it requires already one cell for 30 of Greisheim and for 200 bells of the Bell system. The concentration of the caustic potash is in the cell of Greisheim 6 to 7% and it contains about 12 to 15% KCL, so that for each ton of KOH 96% about 2 tons of KCL have to be separated. The concentration of KOH in the Wilderman Cell is 20 to 22% and the caustic potash is obtained directly pure in the cell. The Greisheim cells are built of iron girders with porous cement diaphragms which are known to live only one to two years, the bells consist also of narrow rectangular boxes made in cement; each of these cells or bells have to be provided with anodes, circulation pipes, gas pipes, etc. and have to be attended to; both systems suffer of necessity from hypochlorides in the brine and have hypochlorides in the caustic.



Current densities for different volts in different Systems. Diagram I

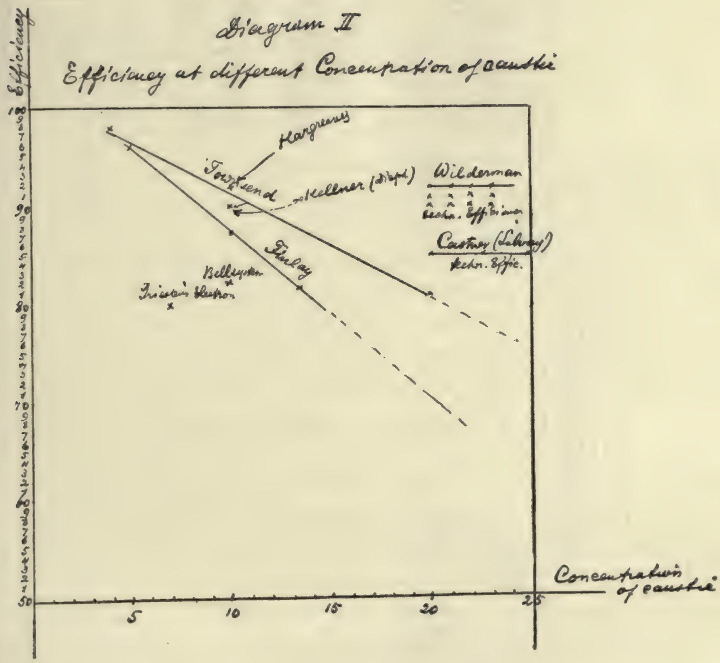
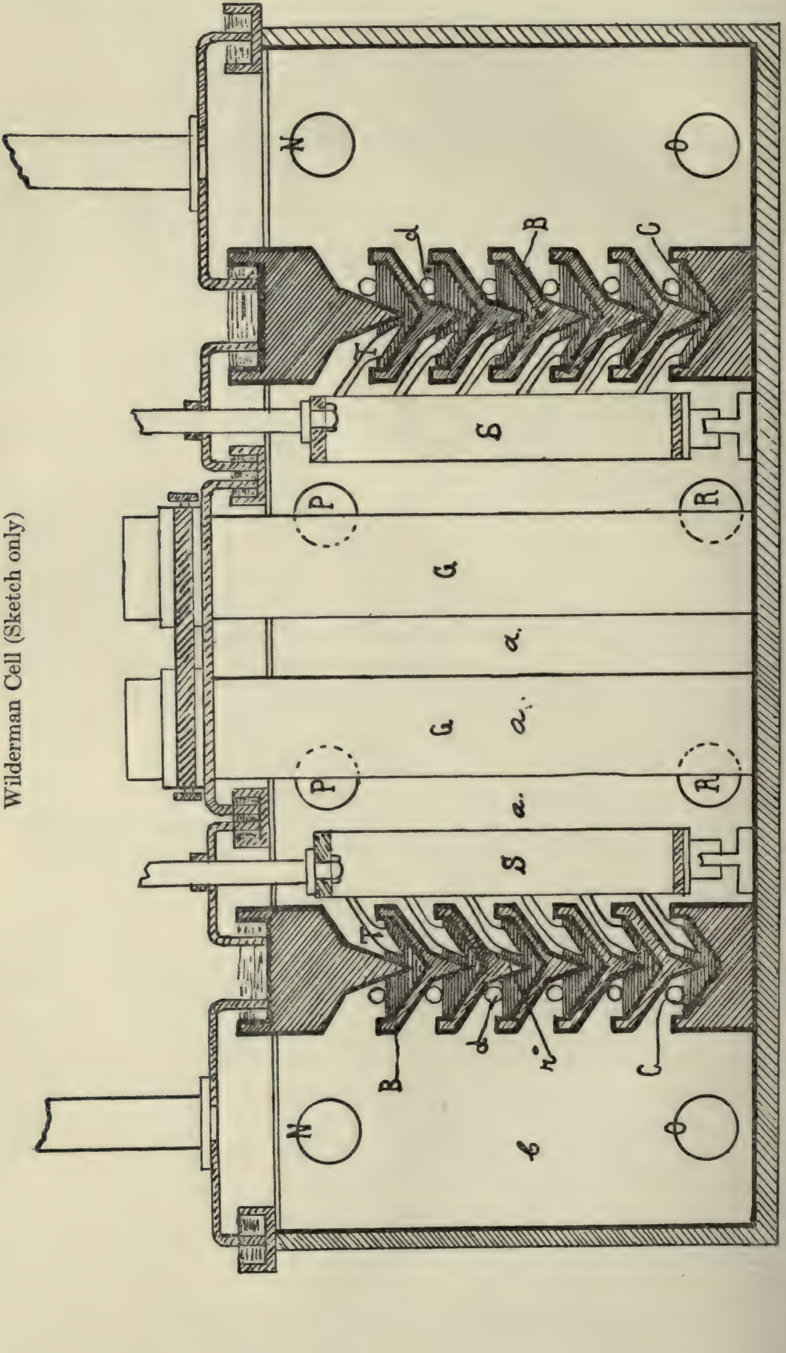


Diagram II
Efficiency at different Concentration of caustic
Efficiency
100
90
80
70
60
50
5
10
15
20
25
Concentration of caustic
Hargreaves
Townsend
Kellner (diaph.)
Wildermann
techn. Efficiency
Castner (Solvay)
techn. Effic.
Finlay
Billiter
Griesheim Electron



Wilderman Cell (Sketch only)

"A PROCESS FOR THE MANUFACTURE OF EBONITES CAPABLE OF RESISTING THE ACTION OF ALKALIS AND CHLORINE, AND ITS EFFECT UPON THE INDUSTRY OF ELECTROLYTIC DECOMPOSITION OF ALKALINE SALTS"

By Dr. M. Wilderman
London, England

For the chemical and electrolytical industry it is of the greatest importance to possess a substance, which is perfectly inert against chemicals and which is cheap and admits a universal application. Such a substance or substances are the ebonites of my invention, which I am now putting before you. Especially in the electrolysis of alkaline salts it is important to possess a substance, which is capable of withstanding alkali and chlorine and also hypochlorides or chlorates. While the different known ebonites can withstand the action of alkali, they are however not capable of withstanding chlorine. Also the so-called Jenkin's mixtures which contain graphite fall to pieces under the action of chlorine. It has already been attempted to produce ebonites capable of withstanding chlorine. The known methods however, employed for this purpose, consisted in the artificial and purely empirical preparation of various mixtures without any chemical or scientific basis, and for this reason the attempts of getting an ebonite capable of withstanding chlorine failed.

There can however be no doubt that we have to deal here with a very complicated chemical problem, and the object of this invention is to solve this problem by the help of scientific considerations, and so to manufacture an ebonite capable of fulfilling the conditions necessary for withstanding the action of chlorine.

Raw rubber is known to be a hydro-carbon of the empirical formula C_5H_8. The investigations of Weber and others made it very probable that the hydro-carbon of raw rubber has the formula $C_{10}H_{16}$, in reality rubber however is a colloid, therefore a polyprene of a very high molecular weight, a multiple of the formula C_5H_8. The investigations of Tilden, Gladstone and Hibbert, Ipatiew and Wittorf made it probable that the polyprene contains two double bonds. Gladstone and Hibbert produced compounds of the composition $C_{10}H_{16}Br_4$ and $C_{10}H_{15}Br_5$, but could not obtain the compound $C_{10}H_{16}Br_6$. Gladstone and Hibbert assumed on the basis of their optical measurements that polyprene contains three double bonds. I have proved however that the first assumption is the correct one and that the polyprene contains two double bonds only. It is impossible so far as is known to combine chemically more than two atoms of sulphur with the polyprene. It thus follows that in case of the product $C_{10}H_{15}Br_5$ four atoms of bromine have saturated two double bonds while the 5th bromine atom has acted by substitution of one of the hydrogen atoms of the $C_{10}H_{16}$.

By the above considerations I have found that to get an ebonite which is capable of withstanding the action of chlorine, it is necessary to prepare it in such a manner that the two double bonds in the polyprene are saturated so that the action of chlorine should be restricted to the slow process of substitution, the process of addition of chlorine to unsaturated compounds being very much more vigorous than that of substitution which is comparatively a very slow one.

In the preparation of soft and hard rubber the sulphur used combines, as known, with the rubber partially chemically while another part of the same remains uncombined. The action of sulphur in the ordinary vulcanisation consists therefore in this that the double bonds of the polyprene are only partially saturated, the more so since the amount of sulphur used is usually smaller than is necessary for the production of a body of the formula $C_{10}H_{16}S_2$. Though in Gutrie's mixture 33% sulphur is used, this mixture is nevertheless only normally vulcanised, that is, the vulcanisation takes from 5 to 8 hours, a time which is not nearly sufficient to produce an ebonite capable of withstanding chlorine, because the double bonds of the hydro-carbon cannot be sufficiently saturated in such a time.

In order to get an ebonite capable of withstanding chlorine it was therefore necessary to saturate the remaining unsaturated bonds of the hydrocarbon either by chlorine or by sulphur. In the first case we get a product which falls to pieces, and for this reason the chlorinated surface does not form a protecting layer for the ebonite and does not prevent the further penetration of chlorine to the ebonite below the same, and therefore the action of the chlorine in destroying the ebonite is rapid and continuous.

In case of sulphur there is no such difficulty and a product can be obtained which is unable to take up chlorine by addition provided the vulcanisation be continued long enough. If the mixture of ingredients in the proportions to produce $C_{10}H_{16}S_2$ is over-vulcanised, which in the ordinary ebonite manufacture is regarded as a wrong vulcanisation, because a number of physical properties such as flexibility and elasticity suffer we get nevertheless a product which is completely uniform and quite coherent. In all cases where the chemical and not the physical properties of the ebonite are of importance, I have found therefore in the over-vulcanisation a means of producing a material which is capable of withstanding chlorine and which is the more capable of withstanding chlorine the more the ebonite is over-vulcanised i.e., the more sulphur combined chemically with the polyprene.

The present invention therefore consists in the production of an ebonite capable of withstanding chlorine by the use of so much sulphur as is required to produce a body of the formula $C_{10}H_{16}S_2$, this mixture being over-vulcanised as much as possible, without unduly impairing such of its physical properties as are necessary.

As known, all raw rubber contains resins in addition to the polyprene. Since the amount of sulphur relative to that of the polyprene in the mixture is of a definite proportion so as to be able to produce the chemical compound $C_{10}H_{16}S_2$, it is therefore necessary that the raw rubber should contain as small a quantity of resins as possible so that the ratio between the amounts of polyprene and sulphur shall be disturbed as little as possible. It is advisable for this reason always to use only good rubber, for instance, Para rubber. If rubbers of a medium quality are used these should not contain more than about 4% of resins.

Since the resins also take up sulphur it is advisable to use somewhat more sulphur than corresponds to the formula $C_{10}H_{16}S_2$, this is also advisable because when sulphur is added the reaction becomes accelerated and is more complete when some excess of sulphur is present.

The products obtained in the above described manner, although improved are not entirely capable of withstanding the action of chlorine. I have therefore investigated whether the products will become more capable of withstanding the action of chlorine, if substances are added to the mixture of rubber and sulphur which are chemically indifferent both to chlorine and to alkali, such as graphite, paraffin, barium sulphate, etc. These substances have previously been used in the ebonite manufacture, but it was necessary for the purpose of this invention to find a substance which not only resists the action of chlorine and alkali, but which does not prove injurious to the ebonite itself, i.e. does not destroy the cohesion of the rubber, or of the ebonite itself. On the other hand, it is desirable to use as much of these substances withstanding chlorine and alkali as possible so that they may more effectually protect the ebonite against the slower action of chlorine upon the ebonite to form substitution products.

It was found that graphite answered this purpose best; I have found that an addition of about 10% of graphite to the rubber leads to the best results. If materially less graphite is taken the life of the ebonite becomes considerably shorter. If materially more graphite is used the ebonite loses more and more its coherence under the action of chlorine and the life of the ebonite is considerably diminished, the surface becoming under the action of chlorine more and more porous and easily falling to pieces. By vulcanising in the manner described above, and adding graphite in the quantity mentioned above, by the combination of these features of the process a product is obtained of an exceptional length of life, upon which chlorine has practically no influence. The advantage obtained with the new product is evident from the fact that, while most ebonites when exposed to the action of chlorine at 65% Centigrade rapidly disintegrate the ebonite produced according to the present invention (when used for covering iron) is capable of withstanding chlorine for many years before one millimeter of the same is destroyed. The ebonites thus obtained belong to the most inert substances, which stand chemicals (acids, alkali, etc.) excellently, and also such substances as hypochlorides or chlorates do not affect the same at all. Even the sulphides such as Na_2S, which are the strongest extractors of sulphur, do not seem to affect the same at all. For the electrolytic alkali industry the possession of such an inert substance, which stands chlorine, alkali and hypochlorides or chlorates perfectly well is of the very greatest importance, as it enables to build electrolytic cells of quite an unusual life, which means an enormous saving in the costs of production, a great saving in repairs, labour, and this reduces also to a minimum the losses in the valuable products made. By covering iron with ebonite of such properties we are able to build cells, which combine the mechanical strength and security of iron with the chemical inertness and life of my ebonites. And this forms a new departure in the construction of electrolytic cells, which up to the present are built in materials, which do not possess the mechanical strength of apparatus, customary to the rest of the heavy chemical industry, and are built of materials which are unable to stand either chlorine or caustic or both.

According to one example, the process is carried out in the following manner:—

10 parts of chemically pure finely divided graphite, 33 parts of sulphur and 57 parts of Para rubber are intimately mixed to a homogeneous mass according to the known method, and the mixture is then used for the preparation of ebonite plates, as well as for covering iron by hand or in moulds in the known manner. The vulcanization is first conducted slowly, and the pressure gradually brought during a period of an hour to two hours to about three atmospheres and then kept at this pressure for a suitable time such as from 40 to 45 hours, until the requisite vulcanisation is achieved.

The proportions given above may be varied and useful products will still be obtained but their results become worse the more we deviate from the given proportions. The speed with which the correct vulcanisation takes place changes naturally with the temperature of vulcanisation. It is greater the higher is the temperature used.

The covering of iron with ebonite takes place in steel moulds, under very great pressure; the methods requisite for this are now worked out to very great perfection and precision. We can cover any piece of iron with ebonite to any desired shape with a precision of 0.1 to 0.2 of m.m., and the ebonite itself can be made to adhere to the iron so perfectly, that we may hammer it without breaking it off from the iron, unless violence is used. (This will be illustrated). The vulcanisation in case of covering of iron with ebonite does not require to be so long, as in the case of pure ebonites, evidently because of the iron being a good conductor of heat.

Generally speaking, the vulcanisation for very good ebonite plates should last for 24 to 48 hours and in case of iron plates covered with ebonite the time of 12 to 24 hours should suffice. In this case the physical properties of ebonite such as elasticity and flexibility, are sufficiently preserved for the purpose. In any case the physical properties become somewhat affected through over-vulcanisation, and the period of vulcanisation should be varied according to the purpose in view in each individual case, and the necessary methods must be used to make the ebonite adhere perfectly to the iron.

THE COMMERCIAL DEVELOPMENT OF CHEMICAL PROCESSES

By Jasper Whiting

Boston, Mass.

There is an old proverb that reads—"It is a wise Father that knows his own child." If this proverb be paraphrased to apply to chemical processes, one might say:—It is a wise scientist who knows his own invention—after it has achieved commercial success. The finished product seldom bears any great resemblance to the original idea. Much has happened to it since it emerged from the brain of the inventor. Like the properly reared small boy, it has been coddled and fostered, encouraged and controlled, whipped into shape and tested in the school of experience, until it has come out a man in stature, containing the blood of its birth, but very different in appearance, character and efficiency. And just as each child, though different from every other child, must pass through certain definite stages in his physical and mental development, so I think, chemical processes, though varying one from another in character and detail, must pass through somewhat similar stages if they are to achieve the dignity of commercial success in the shortest possible time and with the least expenditure of money and effort.

I feel a certain hesitancy in approaching this subject, for I realize that I am speaking to men who have had far greater experience than I as parents of processes and who are, therefore, much better able to speak with authority on a subject so broad, elusive and difficult as this one appears to be. Bachelors and spinsters proverbially talk gliby on the training of infants. It all seems easy to them. Still, though I am less experienced than most of you, I refuse to be classed with such benighted persons, for I have had two wayward children of my brain, who have lived to achieve manhood, but not without causing their devoted father more trouble and heartburns than they can ever repay with dividends.

The two processes to which I refer, both of a chemical nature, were of very different characters. The first related to the manufacture of cement from Blast Furnace Slag. This was conceived in 1895 and developed under my direction until 1901, when a plant costing approximately half a million dollars was placed in successful operation. The second process related to the electrolytic production of chlorine and caustic alkalis. This was conceived in 1905 and was developed under my direction till 1911, when a plant costing one quarter of a million dollars was placed in successful operation. The development of each process occupied, therefore, approximately five years and though the two processes were very dissimilar, one being a chemical engineering and the other an electrochemical engineering problem, the means taken to achieve the final results, the periods of evolution, were much the same in each instance. It has occurred to me that it might be helpful to some of the younger men of our profession if I were to set down a few of the more important steps in the evolution and make some observations relating thereto.

Chemical processes may be divided into two general classes. First, those that are purely chemical, that have to do with a formula or reaction and little else; and second, those that are chemical in principle, but require the use of special apparatus in order to carry them out. With the first class I have had little experience. My remarks, therefore, refer only to chemical processes of the second class, those that are more truly chemical engineering problems than problems in pure chemistry.

The evolution of chemical engineering processes may be divided into five distinct stages, the function of each being different from that of any of the others, though all the stages overlap to a greater or less degree. These stages may be designated as follows:

First: The Beaker or Laboratory Stage
Second: The Small Sized Model
Third: The Life Sized Unit
Fourth: The Semi-Commercial Plant
Fifth: The Commercial Plant.

As I have said each stage is distinct from all the others. Each has its own importance, and none should be slighted if the Inventor desires to obtain commercial success. Experience has shown that as a rule he who tries to jump, say, from the first or second stage to the last, lands in the ditch of failure. It is the purpose of this paper to discuss these stages separately and to point out the special function of each.

First, the Beaker or Laboratory Stage. It is the function of this stage to prove the correctness of the chemical principle involved, the novelty of the process and its commercial soundness.

The inventor is proverbially an impractical optimist. He is inclined to think that the idea which emanates from his fertile brain represents from 90 to 99.9% of the full value of the commercial process. In my opinion the original idea is seldom worth more than 10% or even 5% of the finished process, the remainder representing development work and money. But, of course, the idea itself is an essential to success, just as are the other elements which go to make up the final result. It is important, therefore, that the idea be clarified before much money or time is spent in developing it.

The first step in this direction is to conduct such experiments as may be necessary for a full preliminary study of the technical side of the problem in hand. It is not the function of the Laboratory to produce accurately the condition of practical work, but rather to enable the experimenter to test out fundamental principles on a small scale with a correspondingly small outlay of time and money. The aim should be, therefore, to isolate the idea, to divorce it from any conditions which may be misleading in their effect and also to subject it to severe strains to determine its pluck and endurance. Moreover, the experiments should include a study of the underlying causes of the defects in existing competing processes and their extent and importance. This study of the technical side of the problem is of the first importance as insurance against useless work.

But the function of the first stage is not ended here. The novelty of the process must likewise be investigated by a thorough study of the state of the art in text books, periodicals and Patent Office Records, an undertaking which requires time and patience and not a little self control. In the investigations of the Whiting Cell, more than a thousand references were found, classified and catalogued. And just as important as the search covering the novelty of the process is a study to determine whether the basic commercial conditions surrounding the process are sound, that is, whether the raw materials required are to be obtained at a reasonable price and in sufficient quantities; whether the operation is likely to involve any extra hazardous conditions and whether there is a permanent market of sufficient size and stability for the product. From a practical standpoint it is useless to spend time and money on a process not commercially sound, but this is being done constantly by inventors all over the world. I have personally known of several cases where men have spent years developing a secret process only to find in the end that the market conditions were unsound, a fact easily ascertainable in the beginning. When these three factors have been determined, viz.: the correctness of the principle involved, the novelty of the process and its commercial soundness, it is time to write out a full description of the invention, with attached sketches showing diagrammatically the important points; and this description should of course be dated, signed, and acknowledged before a notary public. Except under very unusual conditions I believe a patent should not be applied for during this stage.

The Second Stage—The Small Sized Model. It is the function of this stage to determine the best conditions of operations.

Such a problem as is being considered presupposes the use of a special apparatus in which the process is to be carried out. It is now time to construct such an apparatus, and in designing it, the aim of the inventor should be to model it, without special reference to the final form of the device, with the idea of obtaining an apparatus in which the process may be worked under a great variety of conditions. In other words the model should be as flexible as possible. For instance in the original design of the model of the Whiting Cell, the compartments in which the salt is decomposed and the amalgam oxidized were made independent of one another and in such a way that the dimensions of each and the relationship of one to another could be varied independently within wide limits. By this means with a single model, we were able to determine the proper size and shape of each compartment, their relationship and the most effective method of operation. It is interesting to note that in this instance the results obtained with the first model have had permanent value. This is not always true. By operating the apparatus under a great variety of conditions, the best procedure can be ascertained and the scope of the invention determined within the limits of the experiments performed.

The small sized model, moreover, should be big enough to permit the manufacture of a sufficient quantity of the product to enable the experimenter to determine its quality. In the laboratory one experiments generally with pure chemicals. In the small model it is well to use commercial materials, the impurities in which often are disturbing factors in the success of the process. As regards the final efficiency of the process under actual conditions of plant operation very little of value can be learned from this model, but much knowledge may be obtained which will aid in the design of the final apparatus and in determining the choice of materials to be used therein. It is well that the work of this second stage be conducted by the inventor himself or at least under his supervision.

Third Stage—Life Sized Unit. It is the function of this stage to determine, so far as possible, the final design of the apparatus.

We all know that chemical processes of the class that is being considered depend as much upon mechanical or electrical details as upon the chemical principle involved. The average inventor of such processes is first of all a chemist, and as such, often underrates the importance of engineering as a factor in his work. It is because of this, because of the fact that the chemist fails, for one reason or another, to seek the aid of an engineer at this critical period of his work, attempting to design and superintend the construction of the Life-Sized Unit himself, that many processes, if not wrecked, are at least greatly delayed in their development. It is no disgrace if a man does not embrace within himself all the knowledge of all the arts. If he is really proficient in one branch of one of the arts or sciences, he need not be ashamed to hold his head high. The business man does not attempt do draw his own contracts, but calls in an attorney for that purpose. Doubtless he could acquire the necessary knowledge to draw these contracts if he gave proper attention to the study of law, but, as a business man, he finds that it is economically to his advantage to concentrate his efforts within his particular field and to call in specialists for special work. Personally, this is the plan that I have always adopted, and much of whatever success may have attended the processes which bear my name is due to the various engineers who from time to time have helped me. Thus the development of the cement process was greatly facilitated by the engineers of the Illinois Steel Company, notably Mr. J. G. Bergquist, of Chicago, and the Electrolytic Cell had the benefits of the criticism and advice of Mr. William Hoopes, of Pittsburg, and Professor C. F. Burgess, of the University of Wisconsin. I am glad to have this opportunity to acknowledge my indebtedness to these gentlemen.

The proper design of the Life-Sized Unit, of course, is of the highest importance, but even if constructed after careful thought and with best advice, it is apt only too often to fail to fulfill completely the expectations of the inventor. Flexibility of arrangement, therefore, should be borne in mind in order that changes may be made in the design as occasion warrants. Moreover, the old model should not be discarded as soon as a defect becomes evident, but should be retained until all of its weaknesses are known. The tendency of the brilliant young inventor, whose ideas come thick and fast (or rather, thin and fleeting) is to discard his first apparatus the moment he sees that a detail of it can be improved and proceed to build a new type which will apparently do the work better, but more often than I care to predict, he will find that the old apparatus had virtues which the new one does not possess and if he retains the old while he develops the new, he will be able later to build a third type which will combine the proven good points of each. "Hold fast to that which thou hast," is a proverb which might appropriately be nailed solidly over the desk of every inventor.

The tendency to hurry over the Third Stage in the evolution of a Process is often almost overpowering. After a few weeks or a few months, as the case may be, the operation of so small a plant becomes tedious and the inventor is apt to chafe at not being able to make more rapid progress. It is evident, however, that defects are much more easily remedied on a single unit than on a great number of units, and the more perfect a process emerges from this stage, the shorter and easier will be the subsequent stages, and more complete the success. Moreover, many chemical processes which work well on a small scale, are failures on a large scale. Thus, in the development of the Electrolytic Cell, the provision made for decomposing the amalgam in the oxidizing compartment, though perfectly satisfactory when applied to the small sized model, proved inefficient and unreliable in the Life-Sized Unit, necessitating much research work and a re-design of the apparatus before the defect was overcome. Likewise, many processes have defects that may be called accumulative. I have known a piece of apparatus to work well for a period of seven months, and at the end of that time develop a defect which made it practically useless. One instance of the result of accumulative troubles is still a clear and tragic memory with me. We had been experimenting for some time with a new process for producing simultaneously three products, two of which if separated one from the other were stable, but if brought together formed an explosive mixture. For a number of months everything had operated well, until at last, a gentleman, who had heard of the process and wished to investigate its merits with a view to its purchase, wrote for permisssion to visit the plant. Great preparations were made for his reception. The floor was swept as clean as the proverbial whistle, the bottles and windows were washed and polished and the records of the past months' work plotted in all their detail to form beautiful and convincing curves. At last our visitor arrived. I can see him now as he walked into the room, a cheery smile upon his face and on his legs a brand new pair of trousers. With poorly counterfeited modesty we showed him our apparatus watching narrowly to see if he were properly impressed. Suddenly there was a tremendous explosion. The air was filled with flying cement and glass. Scalding hot liquid was shot upon us as from a spouting geyser. There was a vision of an unfamiliar figure "beating it" to the door, his clothes steaming, his face a study in terror and disgust. The whole apparatus had blown up and with it went our hopes of a quick reward for our Labors. There was not enough of value left in the room to pay for a ruined pair of trousers.

What happened was this: Slight quantities of the two iniquitous products of our process had for a long time been escaping to a bell-like chamber reserved for other things, until, at the psychological moment a ray of sunlight through the newly washed windows caused them to unite with direful results. The evident moral of all this is: "Never wash your windows."

The Life Sized Unit should be tested and tested and tested again. It is not alone necessary to determine how well it will operate under ideal conditions, but how it will withstand the hard knocks of practice. Any ship will make good progress with a fair wind and a following sea. The apparatus should be overloaded until it actually breaks down. The brain of the experimenter should be racked to devise new means of punishment, new methods of multiplying a hundred fold the severities of actual use. This is the shortest and surest way of determining the pluck, endurance and fool-proof qualities of the device. It is Edison's method and he, of course, is a Past Master at the game.

In my opinion a patent covering the invention should not be applied for until the third stage is about 80% completed and the experimenter knows with reasonable certainty that his process will work and his apparatus has permanent value. A patent drawn at this period is sure to be of real worth. As the idea has passed through the three preliminary stages, it has undergone modifications and changes. Now, however, it is a well formulated, definite, practical fact, a thing to which the inventor is properly entitled to protection. Such a patent is almost always obtainable and seldom vulnerable. The invention has been developed logically and as rapidly as systematic work would permit, therefore it is unlikely that others who started later have overtaken the experimenter in this particular field. Ideas hastily formulated and lightly patented seldom are sufficiently complete to be of value; consequently, interference from them is not to be greatly feared, especially if the statement of conception, made and recorded at the end of the First Stage, is available. Before the patent is issued, the Third Stage will have been completed, the design of the apparatus determined, its efficiency and durability demonstrated and the construction of the Semi-Commercial Plant begun.

Fourth Stage—The Semi-Commercial Plant. It is the function of this stage to determine the efficiency of the apparatus when operated in multiple, and its relation to the necessary auxiliary equipment.

At the beginning of this stage, it is necessary to consider a new and very necessary element for success, money. The first three stages consume large amounts of time and energy, but comparatively little hard cash. Now, however, a considerable sum will be needed to carry the process through the Fourth Stage. Of course, there are many ways of proceeding to get this money, and conditions must govern the final analysis; but I would suggest that there are advantages in the erection of this Semi-Commercial Plant in connection with some going concern, giving certain limited rights to use the process, if successful, in consideration of the opportunities and equipment furnished. Generally this is a safer and more economical arrangement at this stage than to attempt to form a Company for the exploitation of the process and the erection of a small independent plant. The well-oiled machinery of the allied concern, its purchasing department, engineers, its laboratory and workmen, will all be available for the new work, leaving the experimenter free to concentrate on his own special problems.

In the designing of the Semi-Commercial Plant, flexibility of arrangement as regards the auxiliary apparatus should once more be borne in mind. For this reason, hand labor is better than machinery for moving materials, and a number of small motors better than shafting for primal power.

The proper size of this plant depends, of course, upon individual conditions. It should be as small as possible, and still be able to produce enough of its product to permit the testing of its quality under the conditions of actual use. It should be large enough to indicate something of the cost and quality of the labor required for the Commerical operation of the process. The Life Sized Unit was looked after by skilled men. It is now necessary to prove that the process may be operated by ordinary cheap labor. Moreover, the plant should contain a sufficient number of units to enable the experimenter to determine their efficiency under the average conditions of plant operation. A single unit may do very good work when petted and pampered by constant adjustments, but give it its place in a series of units all subject to the gruelling test of "average conditions" and it often falls down. Much can be learned from this little plant, especially as regards the general arrangement of the large plant and the relation of one piece of apparatus to another. These are important points which effect not only the first cost of building the final plant, but also the cost of its operation over an extended period of time, and both factors will aid greatly in obtaining the full measure of benefits to be derived from the development work.

Fifth Stage—Commercial Plant. The conditions to be considered in connection with this final stage are too many and too obvious to be spoken of in this paper. I would only suggest that the plant be laid out on a large and comprehensive scale, but on the sectional basis, and only one section built at first. If this section operates successfully, the development work is over and the process has reached the Promised Land.

The true Scientist who makes investigations for the love of Science cares little for protection of his discoveries. His mind does not concern itself with patents. He desires only to add to the general store of knowledge, to wrest new secrets from Nature for the benefit of his fellow men. He should not forget, however, that if his invention is to become useful to a large number of people, which is the final object of his desire, there must be some inducement offered his less altruistic brothers to take up its commercial development, and this inducement as a rule, is obtained only through the Patent Office.

The average man does not pursue development work except with the hope of material gain. That this view is a proper one is recognized by the Community at large whose laws pronounce that an inventor is entitled to protection and to the fruits of his labor. It is a common belief that the obtaining of a patent procures this protection. This, of course, is by no means true.

A patent is not a protection until the process or device which it covers is proven to be the invention of the patentee and this proof is established only after the Court of Last Resort has passed favorably upon it. It is, therefore, little more than a record of work done and is seldom worth the expense necessary to prove its value. The experienced inventor, therefore, does not rely exclusively, upon patents for protection. It is well to patent certain features of the process after they have become firmly established or certain features of the necessary apparatus, but it seems to me almost always unwise to patent all the details connected with the process or all the features of the apparatus required for its operation. In Germany very few patents, relatively speaking, are applied for, protection being had through secrecy. In this country, patents are obtained with a freedom almost unbelievable, in fact, the habit of patenting inconsequential ideas achieves with many people almost the dignity of an incurable disease. The more reasonable course, I think, is to combine patents with secrecy. When the inventor approaches the fourth stage in the development of his process, and attempts to interest others in his scheme, he will find that the average business man places a higher value upon the intimate knowledge of the process which the inventor has acquired, than upon the patent which is supposed to protect it. It is important, therefore, that this knowledge be conserved, and to this end, the management of the first four stages in the development of the process from inception to and including the Semi-Commercial Plant, should be exclusively in the hands of the inventor and his immediate loyal assistants as by no other means can the details of the operation be effectively controlled. If this is done, the inventor will, upon the completion of the Semi-Commercial Plant, be in a position to ask and obtain excellent terms not only for his patented process as such, but also for the exclusive knowledge which he and his immediate assistants have obtained through a long period of effort.

It will appear to many from what I have said that I am ultra conservative and that the development of the ordinary chemical process might be conducted along more expeditious lines. I have not found this to be true, and, moreover, this opinion is shared by others. I could point out many cases where these rules are followed in their essentials by successful inventors and investigators. It is true that in the early stages conservatism plays a small part in the work. In fact, it is the mind that dares to think along unusual lines, the brain that does not work in channels, which conceives new processes, just as it is the explorer who dares to travel uncharted ways who brings back knowledge of unknown regions beyond. But as a process nears completion a man should become more and more conservative.

The great question as to whether development work pays can never be definitely decided. It all depends upon the point of view. Of the great army of prospectors who examine the vast areas around a newly developed mining camp, the number who "strike it rich" are so few as to be almost negligible, yet they all have had the thrills of anticipation even if they have been a little short of the daily wage. Nearly all of the great explorers, Columbus, Hudson, DeGama and the rest died poor men. Peary, the great explorer of to-day, has few tangible assets to show for his twenty years work in the Arctic. In the Industrial field, Carnegie spoke with authority when he said, "Pioneering does not pay," and the fact that almost every business man of experience shuns any proposition that has experimental features connected with it, proves conclusively that the odds are greatly against success in development work. It may be justly concluded therefore, that from the money standpoint, exploration work as a rule does not pay, but speaking broadly, it does pay in other ways and pay handsomely. I doubt very much if Peary would exchange the memories of the sensations he experienced when he realized that he stood at the "Top of the World," for all the gold in the Bank of England. There is good reason to believe too, that Hall, the modest inventor of the Aluminum process which bears his name, never derived half so much satisfaction from any of the dividends he has since received (and they have been very large) as came to him with the glitter of the first bit of aluminum produced in his student days. Such rewards as these are beyond the power of the Mint to coin.

It is a far cry from the Beaker Stage in a process to Commercial Success. The road is hard and rocky. The material rewards are few but the view all along the way is bright with expectations; for the really great prizes are open to all. I have not attempted to describe this road in its full variety. It would require the super-assurance of a Rough Rider to undertake so difficult a task. Rather, I have tried to point out what appear to me to be the more important landmarks on the main highway, in the hope that by so doing others more experienced and competent than I will be stimulated to present their views.

ORIGINAL COMMUNICATIONS

EIGHTH INTERNATIONAL

CONGRESS
OF APPLIED CHEMISTRY

Washington and New York

September 4 to 13, 1912

SECTION Xb
PHYSICAL CHEMISTRY

VOL. XXII

ORIGINAL COMMUNICATIONS
EIGHTH INTERNATIONAL
CONGRESS
OF APPLIED CHEMISTRY

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SECTION Xb
PHYSICAL CHEMISTRY

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BLUE GELATINE-COPPER

By Wilder D. Bancroft and T. R. Briggs
Cornell University, Ithaca, N. Y.

Copper and the copper alloys such as brass and the bronzes lend themselves very readily to artistic decoration by means of colored superficial films or "patinas." Great as is the variety of colors which may thus be imparted to copper, nevertheless a rich and true blue patina for this metal is practically unknown. It was while seeking such a blue surface film that the electrolysis of copper acetate solutions containing gelatine was first performed. One gram of gelatine was dissolved in 325 ccs. of a 1% solution of cupric acetate and this mixture electrolyzed between carefully cleaned and burnished electrodes of sheet-copper. The electrolysis was continued for five minutes at a cathode, (and anode) current density which varied between 0.15 and 0.45 amp dm_2. The process was carried out at room temperature.

The electrolysis performed, the cathode was found to be covered on its inner surface with a thin, pale brown deposit, which, when rubbed with the fingers was seen to possess a peculiar, slippery surface caused by a very appreciable amount of gelatine deposited simultaneously with the metallic copper. No gas became visible at either pole during the passage of the current.

In itself, this pale brown cathode deposit gave no indication of its peculiar properties and it was by chance only that these were discovered. An electrode, freshly coated with a layer of the gelatine-copper was by an oversight allowed to remain in the solution of copper acetate from which the film of metal had just been deposited and the current was turned off. On removing the electrode from the solution, it was noticed that the brown color originally possessed by the cathode film had given place to a purplish blue of extraordinary brilliance and beauty. This led to further experiments.

A second electrode was then coated with a film of gelatine-copper and, after careful rinsing with cold tap water, immersed in a 5% solution of copper acetate containing no gelatine. Straightway there ensued a remarkable series of color changes upon the surface of the copper deposit; hues of startling evenness and intensity followed each other in regular succession until the electrodes had acquired a magnificent deep-blue coloration. This process we shall speak of as a "development," since it bears a certain resemblance to the development of the silver image in the process of photography.

EXPERIMENTAL

1. *Effect of Gelatine*

After the process of development had been discovered, a more systematic study of the formation and nature of gelatine-copper was undertaken. It then became evident that gelatine must be present in the electrolyte and that this colloid exerted a tremendous influence upon the nature of the cathode deposit. The term "gelatine-copper" was thus justified. The optimum gelatine concentration was found to lie between 0.25 and 0.66 per cent. The electrolysis of copper acetate solutions containing no gelatine failed to give the developable films nor was it possible to substitute other hydrophile colloids such as starch or gum-arabic for gelatine or glue.

2. *Nature of the Electrolyte*

Electrolysis of copper formate, acetate and propionate solutions containing gelatine resulted in cathode films which developed blue in copper acetate although this development was imperfect in the case of the deposits from the formate solution. Copper sulphate solutions of different strengths and varying gelatine content failed absolutely to give developable deposits. Similar results were obtained with solutions of copper nitrate and chloride.

3. *Effect of Temperature*

Variation of the temperature at which the electrolysis was performed led to interesting results. Between 20° and 40° C., the cathode deposit was of the usual pale brown color and gave a more or less satisfactory color-development to blue in copper acetate. At 50° C. or at higher temperatures, the cathode deposit was colored a bright red or a brick red and was unaffected by the developing solution. Between 55° and 60° a short electrolysis with a low current density gave a gold-colored but very thin film which had a rather iridescent appearance. These gold and red films can be lacquered with complete success and are interesting in their application to metallochromy.

4. *Other Factors*

The best results were obtained with copper acetate or propionate solutions made up in the proportion of 1 or 2 parts by weight of the crystallized salt to 100 parts of water. The electrolyte should be neutral or at most but very slightly acid. The current density must be low—between 0.15 and 0.45 amp dm_2—and the process need not exceed 5 minutes in duration. The nature of the metal used as cathode is of little importance as long as the copper solution is not decomposed. Thus with nickel, brass, and platinum, good deposits were obtained as adherent cathode films which developed a good blue color.

5. *The Development of the Blue Color*

A 5% copper acetate solution containing no gelatine was used as the developing bath throughout this work, although a copper propionate solution may also be employed. Copper formate developer gave less satisfactory results. A large number of other salt solutions were then tried as developers with practicably no success. Thus in normal copper sulphate solution a film of gelatine-copper was colored a dull, dark indigo. In N/50 copper sulphate a fairly good blue color was developed although the colors obtained with sulphate solutions are distinctly inferior to those prepared with acetate developer. Very dilute copper nitrate oxidized the film to dark brown copper oxide while a chloride solution spoiled the deposit entirely.

Several oxidizing solutions were next used with negative results. Potassium chromate, bichromate, permanganate, perchlorate, chlorate, and persulphate failed to give even a trace of blue coloration. The films were usually oxidized slowly to brown cupric oxide. Reducing solutions gave no development. The film of gelatine-copper was unaffected by dilute, warm, hydrazine hydrate and underwent accelerated blue development in copper acetate after such treatment.

A solution of sodium acetate gave no blue coloration of the copper film nor was it otherwise with the acetate solutions of other metals. Hence this phenomenon must be a function of the copper contained in the developing solutions.

6. *Reverse Development*

An electrode, covered with a deep blue film, was immersed in a very dilute aqueous solution of hydrazine hydrate and, in a short time, bubbles of nitrogen began to form on the blue surafce. The blue color then slowly faded away, until, passing in the reverse direction through the series of colors previously described, the film of gelatine-copper again took on its original brown color. This process was called a "reverse development."

The reverse development completed, the electrode was rinsed in distilled water and once more immersed in the usual copper acetate developer. The blue color formed again quickly, but was a bit thin and uneven.

If a film of gelatine-copper is allowed to stand undeveloped for several hours, it completely loses its power of developing in copper acetate. This is probably due to its oxidation by the air because it was found that treatment of such a "dead" film with hydrazine hydrate was sufficient to regenerate its powers of development. The same result was obtained with a film after immersion in warm, dilute hydrogen peroxide—no development occurred until the layer of oxide so produced had been reduced with hydrazine.

THEORY AND CONCLUSIONS

Schützenberger, by the electrolysis of copper acetate solutions, obtained at the cathode a peculiar form of copper; and, being unable to explain its unusual behavior, he announced it as an allotropic modification. Wiedemann incorrectly contended that the new form of copper was really the oxide of that metal, while recently Benedicks has advanced the idea that we have to deal with a solid solution of acetic acid in copper. It can be shown, however, by a careful study of their results and by consideration of the facts of colloid chemistry, that the allotropic copper of Schützenberger is merely the normal metal in the form of an irreversible colloid gel.

The same conclusion is applicable to the deposits of gelatine-copper described in this paper. The gelatine acts here as the "protecting colloid," migrates by cataphoresis to the cathode, and there inhibits the growth or crystallization of the copper nuclei. Gelatine-copper is an irreversible gel of colloidal copper. The whole phenomenon is but another example of the marked influence of organic and other colloidal substances upon metals prepared by electrolysis, accounts of which have appeared in the recent papers of Müller and Bahntje, Snowdon, and others.

What is the nature and mechanism of the process of the color development? This is indeed a difficult problem, chiefly because of the exceeding small quantities of reacting material of necessity dealt with. The blue, although a superficial color, is nevertheless not the color of a thin film of gelatine or oxide bringing about interference disturbances in the reflected rays of light. Nor does it seem to be the color of a definite chemical compound. The blue layer does contain oxide as is shown by its action in hydrazine and yet it cannot be prepared by any process of simple oxidation. It cannot be produced by the partial coagulation of the copper gel.

It was shown by Wiedemann that Schützenberger's copper possesses the power of adsorbing very considerable quantities of copper oxide from copper acetate solutions. This observation furnished the clue to the process of development. The color changes that appear upon the film are the result of *a surface adsorption of hydrous copper oxide from the copper solution.* The hydrous copper oxide is present as a suspension in very appreciable quantities in the acetate or propionate solutions, being the product of hydrolytic dissociation. This being the case, we should expect the best development with the acetate solutions and but little color effect with the sulphate and chloride developers.

The reversal of development caused by hydrazine is due to the reduction of the adsorbed oxide. There seems to be a certain definite concentration of oxide in the copper film necessary for the production of a blue color. As the concentration of the oxide increases by continued adsorption, the film passes through the series of colors so distinctive of the development.

In conclusion it can be said in support of this hypothesis that it is in accord with many of the established facts in colloid chemistry and explains in the best possible manner this decidedly obscure phenomenon. Stannic oxide adsorbs gold from suspension and forms the "Purple of Cassius"; under very special conditions colloidal copper adsorbs hydrous copper oxide and similarily gives an intensely colored adsorption compound.

SUMMARY

The electrolytic production of a form of colloidal copper was performed with certain copper solutions containing gelatine.

This new form of copper develops a remarkable series of colors when immersed in certain copper solutions, a peacock-blue being the finest color obtained.

The process of development is an adsorption of hydrous copper oxide by the surface of the colloid film.

There have been described methods of coloring metal objects gold, golden-brown or red.

ALLOTROPY OF IRON AND SILVERIODIDE

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For the metallography of the iron, its allotropy is still the most vital question. Although it seems as though a certain, even if indistinct, agreement has been attained regarding the existence of α, β and $\tau-$iron, there still remains considerable work to be done, even for chemistry in general. It is therefore best that we, first of all, clearly indicate what we mean by allotropy and what different cases are to be taken as possible; after that account for some special determinations on silveriodide, and finally discuss the influence these may have on the opinion about the allotropy of iron.

I. DEFINITION OF ALLOTROPY

Theoretical transformation curves

The properties of a body, whether simple or compound, usually change with the temperature of the body. But sometimes the dependence on the temperature is especially perceptible. At a certain temperature (or at a definite number of temperature points) a sudden transformation of the properties of the body takes place, a change of modification, which according to the customary terminology (Berzelius, 1841) is called allotropy if the body is simple (a chemical element), but polymorphy if it is compound (chemical combination). These definitions are, however, not strictly adhered to (compare J. Meyer, list of literature); in the following, with W. Ostwald, we use the word allotropy for both cases.

We will now try to more precisely express the conditions which may be comprised as allotropy. We only take into consideration ordinary equilibrium (*i.e.*, we presume that the properties of the body are at any temperature and under all conditions independent of time).

Now suppose that we have determined a certain property's quantitative dependence on the temperature. If the curve thus obtained show a point of discontinuity—that is, if at a certain temperature an infinitely small temperature change causes a finite change of the property, we say that the temperature is an allotropic point of transformation for the body in question (strictly: in regard to the property chosen) and the temperature of transition is said to be the limit between two allotropical modifications of the body.

The property which is usually put in the first place is the relation to absorption of heat, its sudden transition usually brings about easily seen changes in the speed of cooling or heating. As a rule such a point of transition is noticed in several properties, but need not be perceptible in all. (The definition given has the same range as it already had with Berzelius, and which J. Meyer still considers the most suitable, *i.e.*, it embraces also those modifications which take place at the transition between the different so-called states of aggregation.)

The chosen property can in the proximity of the point of change be thought to depend on the temperature in four principally different ways:

I. The change from *b* to *c* Fig. 1, I, occurs at the transition temperature T quite suddenly, so that in neither the curve *a-b* for the α-modification nor *c-d* for the β-modification can any deviation be observed from the course "normal" at some distance from T.

The transformation α/β occurs perfectly sharp. There can be no hesitancy here: the transformation takes place sharply at the temperature T. The body alters properties abruptly; there is no continuous transition α/β, which may also be so expressed that the two modifications are insoluble in each other.

This is the ideal case which usually presents itself to the mind as an expression for an allotropical transformation.

II. It may be thought that *one* of the curves *ab* or *cd* diverges more or less from its "normal" course (shown by dots in Fig. 1) when the temperature approaches to T, thereby getting nearer the other curve (Fig. 1, II:a and II:b). The transition α/β is less sharp; we may express this saying that the β-modification has a *limited solubility* in the α-modification, or *vice versa.*

III. It is further possible that both *ab* and *cd* in the proximity

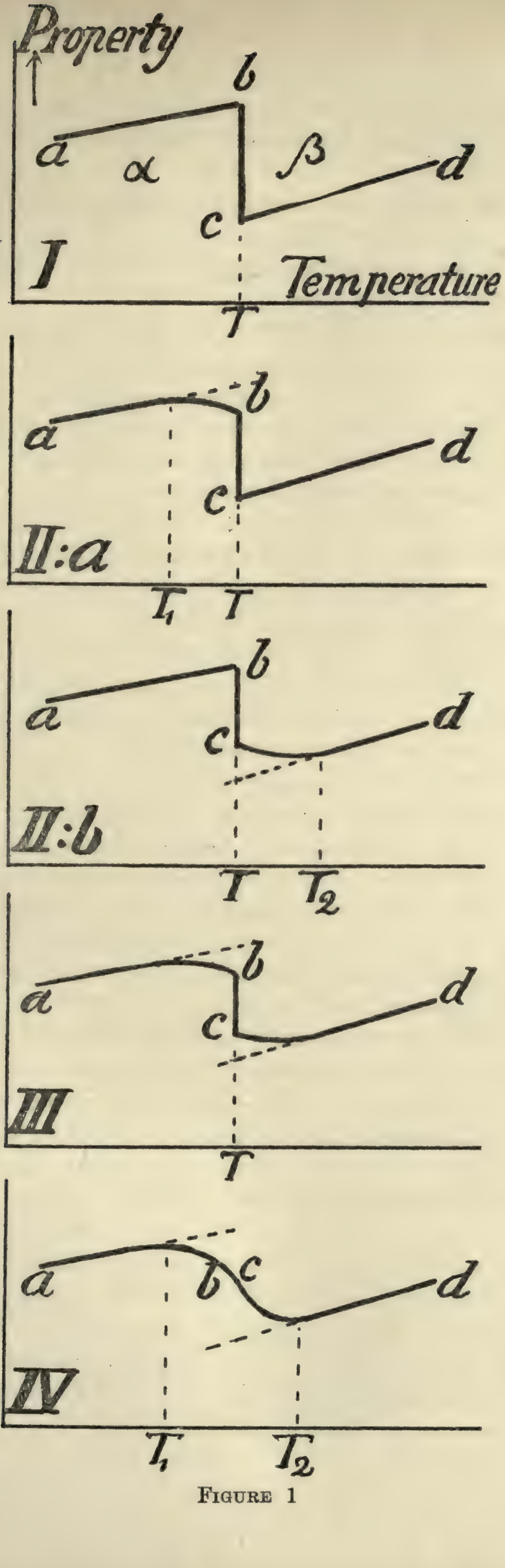
Property
b
a
α
β
d
c
I
Temperature
T
b
a
d
c
II:a
T1
T
b
a
d
c
II:b
T
T2
b
a
d
c
III
T
c
a
b
d
IV
T1
T2

Figure 1

of T diverge from the respective normal course (Fig. 1, III). Hereby the transition α/β becomes still less sharp. In analogy with the foregoing one may say that *both modifications have a limited solubility for each other.*

IV. It cannot be left out of account that the transition between both the normal curves *ab* and *cd* occurs in a *perfectly continuous manner* (Fig. 1, IV). In this case, which may also be said to mean unlimited solubility between the supposed modifications, no allotropic transformation *point* will, in the sense of the definition, be found; but it may be fully justified to speak of a *transformation range* T_1 T_2. Illustrations of this case are to be found in liquid state (for ex. sulphur), and in gases with molecules dissociating at increasing temperature (as gas of iodine); compare also page 26.

We have thus to take into consideration cases I–IV. In the physical chemistry the conviction is gradually working its way in, that *one always has to take into account a certain solubility between two bodies.* Solubility between two modifications of the same body and solubility between two different bodies can not be said to present any principal difference.

One may therefore dare to assert that the most presumptuousless supposition regarding an allotropic transformation is that its course is that of type III, which embraces the others as special cases; afterwards one ought in every case give attention to the experimental determinations of how large the deviations from the normal lines (*ab*, resp. *cd*) may be; or, in other words, to what degree a reciprocal solubility may be supposed.

From the foregoing theoretical transformation curves those obtained by *experimental determinations* will always deviate more or less; it is probably taking great consideration to the faulty sources possible (especially temperature differences), which has been the cause that only case I has nearly always been supposed.

A sure illustration of case I may probably be had in the transformation points at 83° C. and 35° C. for nitrate of ammonium (for which the calculated coefficient of pressure, according to Tammann and Luossana agrees with the observed, see Roozeboom).

A transformation curve of type II:b has been long known, namely for the substance H_2O, where one has been obliged to suppose that the modification ice is to a certain degree soluble on the modification water, whereby the remarkable minimum of volume at 4° C. is explained.

In the following we will find illustrations of case II:a.

II. THE ALLOTROPY OF SILVERIODIDE

The experiments for verifying for silveriodide the well-known Thomson formula for the pressure coefficient for the transformation temperature have, as is known, been unsuccessful.

Tammann found a value that was about 4 times too great, and Mallard and Le Chatelier a still larger value for the pressure coefficient, dT/dp.[1]

Thus: Tammann presumes still another (a third) AgJ-modification, occurring somewhere below the transformation temperature 147° and supposes that the hexagonal modification (stable below 147°) can solve (a certain amount of) the regular (stable above 147°); Roozeboom finds the occurring of the third modification unclear and demands better proofs for the supposed solubility.

As Maxwell in his Theory of Heat, p. 8, has pointed out, silveriodide is acknowledged as the only known body which contracts at increasing room-temperature. I have a long time considered this singular fact as a proof that at increase of the temperature from the room-temperature in the hexagonal modification there arises a small quantity of the regular modification, which according to Rodwell has a considerably lower specific volume (an intense contraction occurring when the temperature rises to 147°).

If this interpretation is correct, one will — as the regular modification may be thought solved in the other only in the proximity of the point of transformation — come to the conclusion that at temperatures lying *considerably below* that of the room-temperature the silveriodide may have a positive, normal coefficient of expansion.

The following *Determinations of the Dilatation of Silveriodide from* −180° *to* +200°, were carried out.

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[1] See Roozeboom's *Die heterogenen Gleichgewichte* I, 130.—I quote Roozeboom in extenso about this: "Tammann (Wied, Anm. 68, 646) hat nun bewiesen, dass dies einer anderen Verwandlung des hexagonalen AgJ zugeschrieben werden muss, *die etwa unterhalb* 100° *auftritt, deren Verhältnisse aber nicht gut aufgeklärt sind.* Er vermutet dass die Abweichung der von 145° ausgehende Kurve vom berechneten Wert durch die Annahme erklärt werden könnte, dass *das hexagonale AgJ mit dem regulären Mischkrystalle bilde.* Bevor eine derartige Annahme zulässig ist, sind jedenfalls deutlichere Beweise erwünscht."

For this purpose a small apparatus of fused silica was constructed, which permitted a mirror-reading of the dilatations (even of as small test-staves as 10 x 1 mm.).

The dilatation apparatus was surrounded by a double-walled cylinder, containing a heating spiral so that the whole could, after having been put into liquid air, easily, by means of a suitable current, be adjusted at any temperatures whatever between that of liquid air and room-temperature.

The temperature was measured with a thermo-element, the junction of which was in close proximity to the test-stave. The test-staves were made by sucking molten silveriodide into thin-walled glass-tubes which had been sooted on the inside (being spontaneously blown off at the cooling at the temperature of

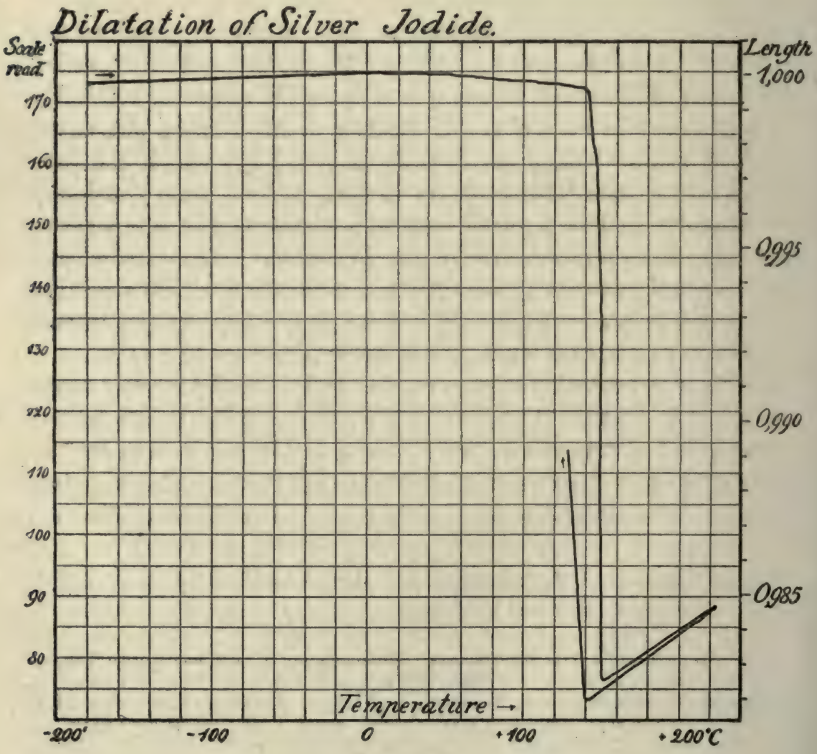

FIGURE 2

transition. Of the two series between −180° C. and +206° C., which agree very well, the one is graphically illustrated in Fig. 2.

From this we infer *that at low temperatures,* at which no earlier measurements have been published, *the silveriodide resembles almost all the other known bodies, i.e.,* that it has a normal, positive coefficient of dilatation.

At increasing temperatures this grows less and becomes 0 in the proximity of 0°. After that a weak contraction gradually takes place, slowly increasing to +140°, when a very sudden contraction occurs, during which the temperature was taken to 149°.[1] After the transformation the mass has a considerably larger coefficient of dilatation. This latter aspect of the curve corresponds very well to that obtained when using the figures published by Rodwell.

The transition of the silveriodide at about 147° thus corresponds to the type II:a.

If the determinations of electrical conductivity, propounded by Kohlrausch are represented graphically (by using a logarithmic scale), you get the impression that these determinations also indicate that the transition progresses continuously from lower temperature to that of the point of transition.

What has now been quoted may therefore be considered to prove that at least one transformation of type II:a is known. Through this Tammann's supposition as to the solubility between the hexagonal and the regular modifications is also confirmed. On the other hand, there seems scarcely to be any reason for accepting the supposition of a third modification, as the properties of that may probably be explained through the solubility just mentioned; in other words: if you persist on a third intermediary modification, the simplest hypothesis will, however, be that it only consists of hexagonal silveriodide, which in solution contains a certain limited amount of regular silveriodide.

III. THE ALLOTROPY OF IRON

Historical

When turning our attention to the iron, we will call to mind the following words of one of the most fundamental investigators in this branch. F. Osmond[1] says: "il est regrettable que les traités modernes négligent l'histoire et présentent commes des monuments achevés des sciences en perpetuelle évolution".

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[1] According to Monkemeyer the point of transition is 146.7°.

The history in this case does not go far back.

Without knowledge of the earlier works of Gore (1869), Barrett (1873), Tait (1873), F. Osmond and J. Werth deposited on July 9, 1883, at the Academy of Sciences at Paris, a sealed manuscript containing all the principal conclusions which later on were given in the work "Théorie cellulaire des propriétés de l'acier" which was published by them in 1885.

Specially through calorimetric measurements showing 5.2 to 15.0% greater content of energy in quenched steel than in annealed the existence of two different allotropic modifications of the iron were considered as surely proved. "α dominating in annealed steel, β mixed with α in quenched steel in varying amount according to hardness." Different physical properties, such as malleability, density, supported the conclusion that allotropy is present.

In the following important work of Osmond: "Transformation du fer et du carbone" (1887), it is for the first time stated that α-iron is soft, β-iron in itself hard and brittle. From cooling-curves taken by means of Le Chatelier's thermo-element (1887) there was, then, evidenced: (1) sudden transformation of Ar_3" at about 890°; (2) a more undecided retardation of the cooling, "Ar_2", at 750–700°. An r inserted means cooling, a c heating, Osmond opined that only the transformation A_3 occurs suddenly as ordinary allotropic transitions at a definite temperature and that A_2, on the contrary, is, though without distinct boundaries, spread over a long interval of temperature. It was therefore supposed that there exist only two allotropic conditions, α and β, but that the transition from the one to the other may be either discontinuous or progressive. In a new work of 1890 Osmond (III) further discusses the nature of Ar_2 and finds it probable that this transformation is simply "the end of Ar_3, retarded by the presence of a little carbon". Between Ar_2 and Ar_3 the metal is a mixture of the two varieties α and β. There is nothing mentioned about a third modification. The cautious reservation with which Osmond hitherto has mentioned Ar_2—the "Achilles-heel" of the theory of allotropy—seemed all the more justified when Roberts-Austen, in the first of the celebrated "Reports to the Alloys Research Committee," 1891, on a photographically registered temperature-time curve, taken on carefully electrolytically purified iron (accurate analysis by E. Riley showed 0.007% C.), found a distinct standstill corresponding to A_3 but no traces of A_2; on a material given by Osmond (with 0.16% C.) Ar_2 appeared, however, even with this less sensible method.

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[1] *Ferrum, poème latin* . . . traduit en vers français par F. Osmond, Paris, 1906, p. 57.

The existence of A_2 was given an unexpected support in a work by Arnold (1894), who considered that he had proved that A_2 surely exists quite independent of A_3, which Osmond had not dared to state up to that time. Even somewhat earlier (1892) Osmond (V) had himself found that the loss in magnetism corresponds to A_2 and not, as he originally supposed, to A_3. Le Chatelier opined (1894) that A_2 and A_3 must be considered clearly differentiated on account of the magnetic behaviour. The magnetic determinations were considered to have received a good support in P. Curie's renowned work on the magnetism of bodies (1895), and when Osmond (VI) published his classical work on the constituents of steel he came to the logical conclusion of the individual existence of A_2: α-iron below A_2, β-iron between A_2 and A_3, and γ-iron above A_3.

Osmond (VII) was, however, not satisfied with regard to A_2, which he discusses in a paper of 1899, with the conclusion: that several facts seem to indicate that the point Ar_2 extends in reality to a much lower temperature than, say, 700°.

A similar opinion against a decisive transformation was also uttered by Howe and the unsuccessful attempt made by Le Chatelier (1899) to find some discontinuity in dilatation-curves corresponding to A_2, may have given rise to doubts regarding the real existence of A_2.

From the crystallographic investigations made by Osmond (VIII, IX) (in conjunction with Cartaud) it was found that the crystalline forms of α and β iron are identical, while that of γ-iron differs.

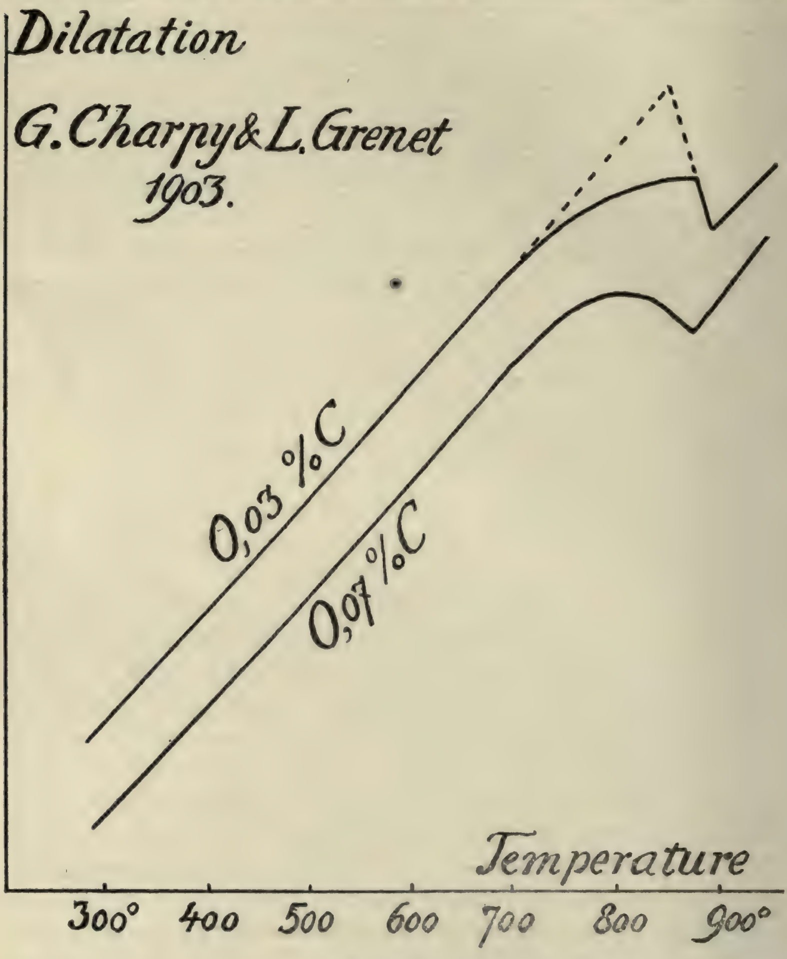

FIGURE 3

Hadfield also declared (1910): "It is doubtful whether any definite facts are available that β-iron exists at all."

In a very clever work of Rosenhain and Humfrey, to which we will later come back, some facts came forth which seemed to be a very strong support for the conclusive existence of A_2 and that the hardness of the iron does suddenly increase within the β-region.

The Present Situation

That A_3 corresponds to an actual transformation point is evident. The question is if A_2 also does so. The most important points favouring this view we will now critically review.

1. The existing cooling-curves show such large divergencies (not mentioned in the preceding), that the thermical determinations cannot be brought forth as proof that A_2 is a transformation point in the sense defined above.

2. After a closer inspection of Curie's determinations using really appropriate graphics (logarithmic scale, as given already by Curie himself) it is evident that an *important* part of the decrease of susceptibility has occurred at a temperature corresponding to A_2 (about 770°) but *by no means to all of it:* the decidedly most prominent magnetical transformation lies, as Osmond first thought, at about 900° or coincides with A_3. The correctness of this is evident from the last work by Weiss and Foëx.

3. If the investigations of Rosenhain and Humfrey be closely analyzed one will, it is true, find that the iron in the β-interval is harder than that within the adjoining α-region, but they cannot serve as a proof that there is any sudden transformation between α and β iron.

From the above it is evident that there is no reason left to prove a discontinuity at A_2. On the contrary, there is an excellent reason for full continuity, namely, the dilatation determinations of Charpy and Grenet, illustrated in Fig. 3, showing that Ac_3 at 890° corresponds to quite a sharp contraction, Ar_2; on the contrary, as I stated in 1904, to a decided though fully continuous digression from the "normal" (dotted) curve.

Our investigations thus give the following results:

The iron shows a perfectly clear transformation point at about 890°, Ar_3; this is distinctly bounded against higher temperatures, but not against lower ones. *The transformation of the iron at 890° thus belongs to the type II: a* which has been shown possible and the actual existence of which has, in the foregoing, been proved for silveriodide.

In accordance therewith A_2 is to be taken in connection with the temperature interval below 890°, within which (on cooling) the dilatation, magnetic properties, etc., have not yet taken the course which is the normal one for the lower temperatures.

By using the nomenclature of Osmond it may be stated thus:

Above the allotropic transition point 890° there is the γ-iron, which does not seem to be able to dissolve any modification existing at lower temperatures.

The modification α-iron, which is stable at lower temperatures, has a certain solubility for the γ-modification which increases with the temperature; at about 750° this solubility is so large that the properties of the iron are *perceptively* influenced by it.

The iron, β-iron, which according to the definition exists between 770° and 890° is to be considered only as *α-iron which in solid solution contains a certain, limited quantity of γ-iron.*

This is in analogy with the presumed third AgJ-modification which is simplest explained as hexagonal AgJ, which in solid solution contains a certain, though limited, quantity of regular AgJ, increasing with the temperature.

It is not difficult to explain that the β-iron nevertheless has quite specific properties, especially hardness; this must depend on the state of solid solution, thereat supposing that another modification acts as foreign matter.

It is thus evident that what is called β-iron possesses some different properties (especially in regard to hardness) from the α-iron. But the question whether the α-iron and the β-iron are different allotropic modifications ought probably to be answered negatively; the question is reduced to this: whether the α-modification in the region T_1 T, Fig. 1, II:a, is to be counted as an allotropic modification, different from the α which exists below T_1.

The opinion expressed here about the β-iron is of a certain interest in connection with the ferronite-hypothesis expounded by the Author in 1904, which from this point of view gains in plausibility and may be said to embrace that at a lower content of carbon (below 0.5% carbon) the ferrite consists of pure α-iron, but at higher percents of carbon, the ferrite consists of α-iron with a certain quantity of dissolved γ-iron, causing a certain solubility of carbon (0.27%). During the last year, the said hypothesis seems to have gotten a valuable experimental confirmation through the calorimetric investigations (cooling-curves) by Arnold.

As regards the widely varying heat-developments which have been noted during cooling, at Ar_2, the explanation of such will probably have to be looked for, as Osmond originally supposed, in the presence of a certain quantity of carbon or other foreign matter retarding the transformation of A_3. A specially significant hint to this is that no development of heat was observed at the investigation (Roberts-Austen) using the purest iron made, analyzed, and up to date.

SUMMARY

1. The very common opinion that *allotropy* means a quite sudden transformation from the one modification to the other can not, *a priori*, be maintained except as a special case (Type I, Fig. 1). There is always the possibility that the one modification (Type II: a and b) or both (Type III) have a certain solubility for the other — this is the simplest expression for the fact that the transformation *partly* takes place continuously. If the solubility were unlimited one could not speak of allotropic transformation point, but allotropic modifications can nevertheless be said to occur. (Type IV.) Which of the types of allotropy (theoretically) possible, that actually occur in each case, must be decided by experimental study of one, preferably more, of the properties in the proximity of and at a sufficient distance from the transition point in question.

2. An experimental study of the dilatation of silveriodide, extended to −180°, has shown that the transformation point of this body at about +147° is an illustration of type II: a. At low temperatures the silveriodide has a *positive* dilatation (Fig. 3, p. 22); only at 0° or room-temperature the well-known *negative* dilatation occurs, that is peculiar to silveriodide. The dilatation must be ascribed to a solubility increasing with the temperature in the hexagonal modification of the regular modification stable above the transition point, a solubility which, according to the curve of dilatation, is in all probability greatly limited.

The supposition of a certain solubility has earlier been made by Tammann, but for want of clear proofs rejected by Roozeboom; determinations of dilatation at higher temperatures have earlier been made by Rodwell, and though only used for the position of the transition-temperature, and coincide very well with those above given.

The simple dilatation apparatus used here and with which temperatures between −180° and 0° could be very conveniently obtained, will probably be of some use on other occasions.

3. A detailed examination of our physical knowledge of the critical transformation point A_3 of the iron at about 890° and the lower, more undecided transformation range A_2, *shows that likewise the transformation of the iron at* 890° belongs to Type II: a, of which we thus know two examples. According to this *the nature of the so-called β-iron is to be α-iron* (*stable at low temperatures*) *containing in solution* a limited amount of γ-iron, increasing with the temperature (stable at temperatures above 890°).

This opinion is greatly a returning to the original views of Osmond.

The standpoint now attained simplifies in a high degree our opinion as to the metallography of iron; this is evident from, amongst other things, that the three theories, now acknowledged as the most probable ones, for the constitution of martensite, when seen from this point of view, *become identical.*

It may be added that a recent interesting note by F. Robin, giving the summary of many properties, raises the question whether or not iron has some allotropic transformations at 100–250° and at 400–500°. Also in this case the things will be simpler by taking into consideration the allotropy exposition expounded here: from Robin's paper, it seems probable that iron, at low temperatures, also has an allotropic transformation range of Type IV (Fig. 1) for which T_1 may be about 100°, T_2 about 400–500°.[1]

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DIE PHYSIKALISCHE NATUR BIOELEKTRISCHER POTENTIALDIFFERENZEN

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Herr Dr. Loeb und der Verfasser haben vor kurzem in dieser Zeitschrift eine Abhandlung betitelt: Uber die Potentialdifferenzen an der unversehrten und verletzten Oberfläche tierischer und pflanzlicher Organe[1], veröffentlicht. In den nachstehenden Zeilen möchte ich eine physikalische Erklärung der in dieser Arbeit gewonnenen experimentellen Ergebnisse zu geben versuchen. Meine Theorie muss sich dabei, soweit sie quantitativ ist, auf die Potentialdifferenzen an der Grenzfläche unversehrter pflanzlicher Organe und wässriger Lösungen beschränken, verletzte Flächen bieten deshalb komplizierte Verhältnisse, weil sie nicht homogen sind.

Der Sitz der bioelektrischen Potentialdifferenzen ist zweifellos an oder in den Membranen zu suchen, d.h. den nicht wässrigen Phasen des Protoplasma welche die Zellen von angrenzenden wässrigen Flüssigkeiten trennen. Dies ist einerseits aus physikalischen Gründen von vorneherein sehr wahrscheinlich und ergiebt sich andererseits aus zahlreichen früheren Untersuchungen.[2] Jede Schnittfläche durch lebendes Gewebe, stellt gewissermassen in elektrischer Bezichung ein Mosaik dar, indem teilweise die Membranen teilweise die wässrigen Flüssigkeiten, die innerhalb und ausserhalb der Zellen sich befinden, zu Tage treten. Eine solche Schnittfläche bietet also in Berührung mit wässrigen Lösungen komplizierte Phänomene: man hat teils Phasengrenzenvon Membran gegen die wässrige Lösungen, teils Grenzflächen der wässrigen Zellularflüssigkeit gegen die wässrige Lösung, und diese beiden Arten von Grenzen verhalten sich elektromotorisch sicherlich sehr verschieden. Ebenfalls komplizierte Verhältnisse bietet die unverletzte tierische Haut, vielleicht auch zum Teil aus anderen Gründen. Die unverletzte Hülle pflanzlicher Organe dagegen kann als aus einer homogenen wasserunlöslichen Phase bestehend angesehen werden, die Potentialdifferenzen, welche sich an derselben bei Berührung mit wässrigen Lösungen bilden, sind scharf definiert und momentan reversibel.

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[1] Biochem. Ztschr. 41, 1 (1912).

[2] Eine Litteratur Zusammenstellung giebt Cremer in Nagels Handbuch der Physiologie. IV Band.

EXPERIMENTELLE TATSACHEN NACH DER FRÜHEREN ARBEIT

Die experimentelle Untersuchung dieser Potentialdifferenzen, insbesondere ihre Abhängigkeit von der Zusammensetzung der wässrigen Lösung ist in der genannten Arbeit ausführlich beschrieben; sie verdient auch ein gewisses Interesse, denn diese Potentialdifferenzen sind wahrscheinlich gleicher oder ähnlicher Natur wie diejenigen an Membranen innerhalb des Gewebes überhaupt, welche für elektrophysiologische Phänomene der verschiedensten Art verantwortlich, einer direkten physikalischen Untersuchung jedoch nicht zugänglich sind.

Ich möchte daher die untersuchten Potentialdifferenzen der Kürze halber als bioelektrische (abgekürzt b. D. P.) bezeichnen. Das für die folgende Untersuchung wichtigste Resultat der früheren bezüglich derselben kann folgendermassen zusammengefasst werden.

Die b. T. D. (an Grenze einer unverletzten Pflanzenteils gegen die wässrige Lösung eines Alkali — oder Erdalkalisalzes) ist von der *Konzentration der Lösung in der Weise abhängig, dass Verdünnung der Lösung dieselbe positiver macht.* Alle Alkali und Erdalkalisalze und auch alle anderen Elektrolyte zeigen ein solches Verhalten, soweit sie nicht stark giftig, d. h. chemisch verändernd auf die Oberfläche der Pflanze einwirken. Die Anderung der Potentialdifferenz ist in dem gleichen Sinne, diejenige an der Phasengrenze Beliebiges Metall | Metallsalzlösung wechselnder Konzentration. Man kann also sagen, dass die b. P. D. *für Kationen reversibel sind,* und zwar *in merkwurdigem Gegensatz zu den bisher bekannten Potentialen für Kationen jeder Art.* Die Grösse der Anderung ist in einem gewissen Konzentrationsbereich beinahe so gross wie nach der Nernst'schen Formel für Potentialdifferenzen $\left(E = \frac{RT}{nF} \ln c + \text{const.}\right)$ zu erwarten ist. Geht man von kleinen Konzentrationen der Salzlösung, etwa 1/1000 molekular, aus und erhöht die Konzentration stufenweise in geometrischer Reihe, z. B. durch Verdoppelung, so findet man dass die Veränderung der b. P. d. etwa 0.058 lg 2 ist bis die Konzentration auf etwa 1/50 mol. gestiegenist; über 1/50 mol. wird die Anderung erheblich kleiner, ist die Konzentration auf 1/2 bis 1/1 mol. gestiegen, so hat weitere Erhöhung keinen Einfluss. *Mit steigender Konzentration strebt also die b. P. D. einem Grenzwert zu.*

SCHEINBARE ABWEICHUNG VOM NERNST'SCHEN GESETZ BEI KLEINEN KONZENTRATIONEN

Erniedrigt man die Konzentration unter 1/1000 molek. so findet man ebenfalls Abweichungen von der Nernst'schen Formel. Diese Abweichungen sind indes nur scheinbar und dem Umstande zuzuschreiben, dass bei Konzentrationen von 1/1000 bis 1/100000 molekular die elektrolytischen Verunreinigungen des destillierten Wassers mit ins Spiel kommen. Das zu diesen Versuchen benutzte destillierte Wasser hatte schätzungsweise nach seiner Leitfähigkeit einen Ionen Gehatt von 1/10000 bis 1/100000 wechselnd. (Eine weitere sorgfältige Reinigung hatte keinen Zweck, da in Berührung mit der Blatt-oder Frucht Oberfläche stets eine Erhöhung der Leitfähigkeit erfolgte.) Da bei den b. P. D. alle Elektrolyte in gleichem Sinne bei Konzentrationsänderung wirken, kann auch die Wirkung der verunreinigenden Ionen nicht vernachlässigt werden. Kontrolliert man durch Leitfähigkeitsbestimmungen die wahren Ionen Konzentrationen, so findet man die Nernst'sche Formel bis zu den höchsten Verdünnungen bestätigt, wie folgendes Beispiel zeigt. Die Kette.

Kalomel Elektrode 1/10 n KCl | Apfel $\underset{a}{|}$ 1/500 KCl Kalomel Elektrode zeigte die E.M.K. 0.064 Volt (2^1 konstant). Wurde die 1/500 KCl — Lösung durch eine 1/1000 n KCl — Lösung ersetzt so war die E.M.K., entsprechend der Anderung der b. P. D. bei *a* 0.082 Volt Diff.: 0.018 Volt, nach Nernst's Formel ber, 0.058 lg 2=0.0175 Volt, also vorzügliche Ubereinstimmung. Leitfähigkeitsbestimmungen ergaben, dass die Konzentration der Lösung durch Verunreinigungen nicht beeinflusst war. Wurde darauf die Konzentration der KCl — Lösung bei *a* durch fünf fache Verdünnung auf 1/5000 erniedrigt, so war die E.M.K.: 0.110 Volt, Differenzen gegen 1/1000 n KCl, 0.028 Volt, Nernst's

Formel giebt 0.058 lg 5 = 0.040 Volt. Diese Abweichung wird verständlich durch Messung der Leitfähigkeit der scheinbar 5000 n KCl — Lösung. $K_2|^\circ$ gemessen 0.0000378, berechnet nach Kohlrausch 0.0000258. Nimmt man an, dass die verunreinigenden Ionen bezüglich Wanderungsgeschwindigkeit sich wie das KCl verhalten, so wäre die wahre Konzentration der 1/5000 n KCl — Lösung $\frac{378}{258}\cdot\frac{1}{5000}=\frac{1}{2940}$, Differenzen der E. M. KK. bei 1/1000 und 1/2940:

$$0.058 \lg 2.94 = 0.0272 \text{ Volt Gefunden } 0.028 \text{ Volt.}$$

Diese scheinbare Abweichung hat hiernach mit besonderen Eigentümlichkeit der b. P. D. nichts zu tun, ist vielmehr nur ein anderer Ausdruck der Tatsache, dass alle Kationen die b. P. D. im gleichen Sinne Beeinflussen. Anders liegt es bei den Abweichungen von der Nernst'schen Formel bei hohen Konzentrationen. Diese können nicht etwa durch Zurückgehen der elektrolytischen Dissoziation bei hohen Konzentrationen erklärt werden. Der Grenzwert der b. P. D. wird bei einer Konzentration von 1/2 mol. bis 1/1 mol. erreicht, auch bei weiterer Konzentrationssteigerung muss aber die absolute Ionen Konzentration offenbar trotz des Zurückgehen des Dissoziationgrades steigen. Die Unveränderlichkeit der b. P. D. in diesem Gebiete zeigt, dass besondere Eigentümlichkeiten der Membran in Spiel sind.

ELEKTROMOTORISCHES VERHALTEN VON SYSTEMEN MIT ZWEIN UNMISCHBAREN ELEKTROLYTISCHEN PHASEN

Das Zustandekommen von Potentialdifferenzen, wie der b. P. D., kann Physikalisch auf zwei verschiedenen Wegen erklär werden. Auf jeden Fall ist es Voraussetzung, dass eine wasserunlösliche Phase (in diesem Falle die Schale oder Membran des Pflanzenteils) neben wässriger Lösung von Bedeutung ist. Es seien zunächst die allgemeinen physikalischen Tatsachen über das Zustandekommen von Potentialdifferenzen in Systemen mit zwei elektrolytischen Phasen besprochen.

Nernst hat zuerst das elektromotorische Verhalten von Systeme mit zwei unmischbaren Phasen experimentell und theoretisch untersucht. Gemeinsam mit Riesenfeld[1] untersuchte er Anordnungen wie.

Verdünnte wässrige Lösung eines beliebigen Salzes z.B. $AgNO_3$ | Phenol | Konzentrierte wässriege Lösung desselben Salzes ($AgNO_3$)

1 2

Zwei Arten von Potentialdifferenzen sind in diesen Ketten zu unterscheiden.

1. "*Diffusionspotentiale*" *in dem Phenol.* Diese kommen zu Stande, wenn die betreffenden Salze eine erhebliche Löslichkeit in dem Phenol besitzen, so dass *die Stromleitung durch die Phenolschicht vermittels der gelösten Salze, resp. deren Ionen, vor sich geht.* Unmittelbar an den Phasengrenzen 1 und 2 besteht nun Verteilungs — Gleichgewicht, das Phenol enthält bei 1 eine kleine, bei 2 eine grosse Konzentration an $AgNO_3$. In der Phenolschicht besteht also ein Konzentrations-Abfall, die Anderung des Potentials längs desselben ist gegeben durch die Funktion:

$$\frac{u-v}{u+v}\,\frac{R\,T}{n\,F}\ln\frac{c_2}{c_1}.$$

In wässrigen Lösungen sind u und v meist ungefähr gleich gross und deshalb die Diffusionspotentiale stets klein, in dem Phenol liegen ähnliche Verhältnisse vor. Nimmt man jedoch an, dass in manchen nicht wässrigen Phasen wie z. B. den Membranen erhebliche Unterschiede in der Wanderungsgeschwindigkeit der positiven und negativen Ionen bestehen, so könnte die Art von Abhängigkeit der b. P. D. von Konzentrationen, wie sie hier beschrieben ist, auftreten. Ist z. B. v in der Membran gleich Null, so wäre das Diffusionspotential gleich $\frac{R\,T}{n\,F}\ln\frac{c_2}{c_1}$. Ich möchte jedoch diese Deutung aus folgenden Gründen für nicht sehr wahrscheinlich halten.[1]

Die Erklärung setzt voraus, dass die Stromleitung durch die zweite Phase (Membran) *ausschliesslich* durch die Salze, welche aus der wässrigen Lösung in die Membran eintreten, vor sich geht. Nun sind wie sich aus osmotischen Versuchen ergiebt die Membranen sehr schwer durchgängig für Salze. Nur äusserst geringe Salzspuren dringen also in die Membrane selbst unter den günstigsten Bedingungen, d. h. wenn die Salzlösung am konzentriertesten ist, ein. Die Leitfähigkeit der Membran müsste durch diese Salzspuren bedingt sein und würde auf Null zurückgehen, wenn die Membran nur mit Wasser umspült ist. Dies ist im hohen Grade unwahrscheinlich, die Membran besitzt wahrscheinlich einen sehr geringen Gehalt an elektrolytischen Ionen, welche unabhängig von den *eingedrungenen ist, und da die Konzentration der letzteren sehr gering ist,* NICHT *neben ihnen vernachlässigt werden kann.*

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[1] Nernst u. Riesenfeld, Annaben der Physik, *8*, 600 to 609.

Ferner ist es mit dieser Annahme kaum verständlich, weshalb die b. P. D. bei hoher Konzentration einem Maximum zustreben, es müssten weitere komplizierte Hilfsannahmen zu diesem Zweck gemacht werden; dabei hat die Annahme extrem differenzierter Ionen Wanderungsgeschwindigkeiten schon an und für sich einen stark hypothetischen Charakter. Ich glaubte diese Erklärungsmöglichkeit hier nur deshalb diskutieren zu müssen, da physiologische Forscher den Verletzungsstrom auf diese Art zu erklären versucht haben. Auch diesen Theorien ist eine gewisse Unsicherheit kaum abzusprechen.

Die andere Art von Potentialdifferenzen, welche in der Nernst-Riesenfeld'schen Kette möglich ist, hat ihren Sitz an der *Phasengrenze selbst.*

Nernst[1] selbst hat vor längerer Zeit gezeigt, dass Phasengrenzpotentiale zwischen elektrolytischen Leitern in derselben Weise wie Potentiale an Metal-Elektrolytgrenzen von der Ionen Konzentration abhängig $= \frac{RT}{nF} \ln \frac{c_1}{c_2} + \text{const.}$, wo c_1 resp. c_2 die Konzentration eines beliebigen *beiden Phasen gemeinsamen Ion in den beiden Phasen bedeutet. Diese für die Elektrochemie fundamentale Tatsache beweist man am besten mit Hilfe einer fiktiven Kette wie*

Metall		Phase I Salz des Metalles enthaltend		Phase II Salz des Metalles enthaltend		Metall
	1		2		3	

Die Phase I und II sowie das Metall befinden sich im Gleichgewicht und somit ist irgend eine chemische (oder physikalische) Reaktion in einer solchen Anordnung nicht möglich, auch nicht bei Stromfluss durch das System. *Die Summe der drei Potentialdifferenzen bei 1, 2 und 3 muss somit gleich Null sein.*

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[1] Nernst, Zeitschr. physik. Chem. *9*, 137, 1892.

Da Pot. Diff. bei $1 = \frac{RT}{nF} \ln c_1 + \text{const.}_1$

und Pot. Diff. bei $3 = \frac{RT}{nF} \ln c_2 + \text{const.}_2$ in entgegengesetzer Richtung so ergiebt sich

für P.D. bei $2 = \frac{RT}{nF} \ln \frac{c_1}{c_2} + \text{const.}_1 - \text{const.}_2$

In einer Kette wie der Nernst-Riesenfeld'schen kommt diese Abhängigkeit des Phasengrenzpotential von der Konzentration nicht zum Vorschein, weil $AgNO_3$ in Wasser und Phenol löslich ist und das Phenol keinen weiteren Elektrolyten enthält.

Für das Dissoziationsgleichgewicht im Wasser gilt:

$$C_{Ag}^{\cdot} C_{NO_3}^{\prime} = K_1 C_{AgNO3}^{n}$$

Für das Dissoziationsgleichgewicht im Phenol gilt:

$$C_{Ag^{\cdot}} . C_{NO_3}^{\prime} = K_2 C_{AgNO_3}^{n}$$

Nach dem Verteilungssatz gilt, da an der Phasengrenze selbst stets Gleichgewicht herrschen muss:

$$\frac{C_{AgNO3}}{C_{AgNO3}} = K_3$$

Division der beiden ersten Gleichungen gibt:

$$\frac{C_{Ag}^{\cdot}}{C_{Ag}^{\cdot}} . \frac{C_{NO_3}^{\prime}}{C_{NO_3}^{\prime}} = \frac{K_1}{K_2} . K_3 = K$$

$$\text{Da} C_{Ag}^{\cdot} = C_{NO_3}^{1} \text{ und } C_{Ag}^{\cdot} = C_{NO_3}^{1},$$

$$\frac{C_{Ag}^{2\cdot}}{C_{Ag}^{2\cdot}} = K \qquad \frac{C_{Ag}^{\cdot}}{C_{Ag}^{\cdot}} = \sqrt{K}.$$

Das Phasengrenzpotential ist also: $\frac{RT}{nF} \ln \sqrt{K} + \text{const.}$ d.h. von der Ag = Konzentration unabhängig. Eine Konzentrationserhöhung im Wasser bringt eben eine solche im Phenol mit sich, und das Verhältnis $\frac{C_{Ag}}{C_{Ag}}$, auf das es für die Potentialdifferenzen ankommt, bleibt unverändert. Dies ist auch der Fall, wenn der Elektrolyt in der einen Phase weitgehender als in der anderen dissoziiert ist, vorausgesetzt, dass das Verteilungsgesetz in der hier angewandten einfachen Form gilt. Anders verhält es sich, wenn die Ionen Konzentrationen der beiden an einandergrenzenden Phasen sich nicht gegenseitig beeinflussen. Dies ist z. B. der Fall in der von Haber[1] zuerst untersuchten Potentialdifferenz

$$\underset{\text{fest}}{\text{AgCl}}\;\Big|\;\text{AgNO}_3-\text{Lösung oder allgemein}$$

$$\text{Unlösliches Salz}\;\Big|\;\begin{array}{l}\text{Lösung eines Salzes mit}\\ \text{einem gleichen Ion.}\end{array}$$

Die Ag Konzentration in der Schicht des festen AgCl ist natürlich völlig unabhängig von der Ag Konzentration der wässrigen Lösung. Nach der Nernst'schen Formel ist die Potentialdifferenz gleich zu setzen

$$\frac{R\,T}{n\;\,F}\ln\left(\frac{C_{Ag^{\cdot}}\text{ in }A_gCl}{C_{Ag^{\cdot}}\text{ in }A_gNO_3\text{ Lösung}}\right)+\text{const.}$$

da $C_{Ag^{\cdot}}$ im AgCl konstant bleibt, folgt somit, dass diese Potentialdifferenz sich wie eine solche an einer metallischen (Ag) Elektrode ändert, was sich experimentell bestätigen liess. Die Phasengrenzformel ist so einer direkten Prüfung zugänglich.

ANWENDUNG DER PHYSIKALISCHEN ERGEBNISSE AUF DIE B. P. D.

Die b. P. D. verhalten sich nun im Gebiet der kleinsten Konzentrationen 1/100 n und weniger wie die Phasengrenzpotantiale vom Typus AgCl | $Ag^{\cdot}$ haltige wässrige Lösung, im höchsten Konzentrationsgebiet (ca. 1/2 n oder mehr) wie die Phasengrenzpotentiale der Nernst-Riesenfeld'schen Kette. Das dazwischen liegende mittlere Konzentrationsgebiet verhält sich wie eine Ubergangszone zwischen diesen beiden Extremen.

Eine befriedigende Erklärung dieses Verhaltens gelingt mit Hilfe der Annahme, dass die Membran einen *Eigengehalt an Elektrolyten* besitzt, d.h. wasserunlösliches Salz in homogener Mischung enthält. Ferner nehemen wir an, dass die Alkali-Salze in der Membran eine kleine, aber endliche Löslichkeit besitzen.

Es sei das wasserunlösliche Salz in der Membran mit Y X bezeichnet (Y^1Anion, X^1Kation), die wässrige Lösung enthalte KCl als Elektrolyt. Ferner nehmen wir an, dass YX mit dem in die Membran eingedrungenen KCl, nach einer vollständig verlaufenen Gleichung reagiert etwa so, dass elektrolytisch dissoziiertes KX und undissoziiertes Y Cl entsteht.

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[1] *Haber*, Ann. d. Physik [4] *26*, 947 (1908). An dieser Arbeit war der Verfasser eben falls beteitigt.

$YX + KCl \rightarrow KX + YCl$

weitgehend dissoziiert wenig dissoziiert oder im Wasser leicht löslich, so dass es aus der Membran ausgelaugt wird.

Oder es könnte folgender Umsatz stattfinden:

$YX + KCl \rightarrow YX\,Cl\,K$

Diese Additionsverbindung sei in die elektrolytischen Ionen YX Cl^1 einerseits, K^1 andererseits dissoziiert (also in derselben Weise wie Platinchlorid-doppelsalze). Beide Annahmen sind für unseren Zweck gleichwertig; sie sind geboten angesichts der Tatsache, dass die Reversibilität der b. P. D. gegenüber *allen* Kationen besteht.

Diese Annahme vom Umsatz gewisser Bestandteile des Gewebes mit Salzen in wässriger Lösung ist übrigens durchaus nicht völlig neu, vielmehr in ähnlicher Weise auf Grund ganz anderer Beobachtungen vor langer Zeit schon von J. Loeb ausgesprochen worden. Loeb beobachtete, dass die Reizbarkeit sowie die rhytmische Bewegung von Muskeln in gemischten Salzlösungen reversible, von der Natur des *Kations* abhängige Anderung erfuhr; z. B. hebt Zusatz von sehr geringen Mengen von Ca^1 zu Na'-Lösungen die rhytmischen Bewegungen auf, ähnliche reversible Wirkungen lassen sich mit Anionen *nicht* beobachten. *Loeb*[1] "stellte sich deshalb vor, dass die Metalle oder Metallverbindungen in den Geweben mit bestimmten organischen Stoffen wie festen Säuren oder Eiweisskörpern verbunden sind, und dass die Substitution eines Metalles für ein anderes die physikalischen Eigenschaften dieser Verbindungen ändert, z. B. Oberflächenspannung, die Viskosität, das Wasserabsorptionsvermögen und den Aggregatzustand. Die Lebenserscheinungen und die Erscheinungen der Reizbarkeit hängen davon ab, dass gewisse Eiweissverbindungen oder Metallseifen in bestimmten Verhältnissen in den Geweben vorhanden sein müssen."

Diese Annahme wird durch die Resultate der vorliegenden Arbeit vollauf bestätigt, obgleich dieselben auf einem wesentlich anderen Gebiet liegen.

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[1] Dynamik der Lebenserscheinungen, p. 120.

Ferner ist folgende für die Theorie vereinfachende Schlussfolgerung geboten. Bei genügend verdünnter Lösung ist, wie wir gesehen haben, die Nernst'sche Formel für b.P.D. innerhalb eines weiten Konzentrationsgebietes in der gleichen Weise wie für Elektrodepotentialdifferenze gültig, nämlich b.P.D. $= \frac{RT}{nF} \ln C$ nüppr. Lösung + const.

Dies ist mit der gemachten Annahme nur dann zu vereinigen, wenn der Umsatz nach irgend einem der genannten Schema vollständig vor sich geht, das heisst, von der Konzentration des Salzes in der wässrigen Lösung im wesentlichen unabhängig ist. Nach dem Verteilungssatz ist andererseits die Konzentration des KCl in der Membran, von der wässrigen KCl Konzentration abhängig, und wir nehmen an, dass das Verteilungsgesetz in der einfachsten Form gilt, dass also Proportionalität der wässrigen und der Membran-Konzentration besteht.

Bei kleinen wässrigen Konzentrationen ist die KCl Konzentration in der Membran so klein, dass sie neben der K^1 Konzentration, welche durch den Elektrolyt-Eigengehalt der Membran bedingt ist, vernachlässigt werden kann. Offenbar ist hiermit die Bedingung einer Veränderlichkeit der b. P. D. nach der Art der Potentialdifferenz AgCl | Ag^1-Lösung gegeben. Bei den höchsten wässrigen Konzentrationen dagegen steigt die KCl-Konzentration der Membran so weit, dass nunmehr umgekehrt der K^1 Eigengehalt der Membran vernachlässigt werden kann; das würde offenbar eine Veränderlichkeit der b.P.D. nach Art der Potentialdifferenz $AgNO_3$ in Phenol | $AgNO_3$ in Wasser zur Folge haben, wie sie tatsächlich beobachtet wird.

ANALYTISCHE FORMULIERUNG DER BESCHRIEBENEN HYPOTHESE

Zur Darstellung der gegenseitigen Abhängigkeit der Ionen Konzentrationen in Membran und wässriger Lösung benutzen wir die üblichen und bewährten Vorstellungen der elektrolytischen Dissoziation und des beweglichen Gleichgewichts.

Membran Wasser c bezeichne Konznetrationen in
$KX = K^1 + X'$ wässriger Lösung.
$KCl = K^1 + Cl^1$
$KCl = K^1 + Cl^1$ C Konzentrationen in der Membran.

Wir nehmen an, dass für die elektrolytische Dissoziation des KCl in Wasser und Membran des Massenwirkungsgesetz in der gleichen Weise angesetzt werden kann, nämlich:

$$C_{K\cdot} C_{Cl}' = K_l C_{KCl}^{\,n1}$$

also entsprechend

$$C_{K\cdot} C_{Cl}' = K_2 \, C_{KCl}^{\,n}$$

(Die Konstanten K_1 und K_2 sollen nicht gleich sein, wohl aber die Exponenten von C_{KCl} und $C_{KCl\cdot}$.)

Das Verteilungsgesetz setzen wir an in der einfachen Form:

$$\frac{C_{KC_l}}{C_{KCl}} = K_3$$

Division der beiden ersten Gleichungen und Substitution mittels der dritten ergiebt:

$$\frac{C_K}{K} = \frac{K_1}{K_2} \cdot \frac{1}{K_3} \frac{C_{Cl}'}{C_{Cl}'}$$

$$= \frac{1}{K} \frac{C_{Cl}'}{C_{Cl}'} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{I}$$

Nach der Regel der Elektroneutralitat ist

$$C_{K\cdot} = C_{Cl}' = C \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{II}$$

$C_{K\cdot} = C_{Cl}' + C_X$[1]

oder $$C_{Cl\cdot} = C_{K\cdot} - C_{Cl}' \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{III}$$

II und III substituiert in I giebt

$$\frac{C}{C_{K\cdot}} = \frac{1}{K} \cdot \frac{C_{K\cdot} - C_X'}{C}$$

$$C_{K\cdot}^2 - C_X' C_{K\cdot}^X = K \, C^2$$

$$C_{K\cdot} = \frac{C_X'}{2} \pm \sqrt{\frac{C_X'^2}{4} + K \, C^2}$$

Von den beiden Lösungen der quadratischen Gleichung hat nur die jenige mit positivem Vorzeichen vor der Wurzel einen physikalischen Sinn. Da nämlich K sowohl als auch C^2 nie einen negativen Wert annehmen können, muss der Wert der Wurzel notwendigerweise grösser als $\frac{C_X'}{2}$ sein; bei negativem Vorzeichen würde dies bedeuten, dass $C_{K\cdot}$, eine Konzentration, negativ ist, eine physikalische Unmöglichkeit! Es ist also

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[1] Dies ist die Empirische Form des Massenwirkungsgesetzes (oder Verdünnungsgesetzes) nach van't Hoff und Rudlolphi.

$$C_{K\cdot} = \frac{C_X'}{2} + \sqrt{\frac{C_X'^2}{4} + KC} \ldots\ldots\ldots\ldots \text{IV}$$

Nach der zitierten Nernst'schen Formel ist die b. P. D. =

$$\frac{R\,T}{n\,F} \ln \frac{C_K}{C_K} + \text{const. oder } \frac{R\,T}{n\,F} \ln \frac{C_K}{C} + \text{const.}$$

Substituiert man für $C_{K\cdot}$ den Wert aus (IV so ergiebt sich

$$\text{b.P.D.} = \frac{RT}{n\,F} \ln \frac{C_{X'}}{2c} + \sqrt{\frac{C_{X'}^2}{4c^2} + K} + \text{const} \ldots\ldots\ldots \text{V.}$$

Halten wir an unserer Annahme fest, dass die elektrolytische Dissoziation in der Membran ähnlich der in Wasser ist, so kann C_X in erster Annäherung als unabhängig von C (wäss. Konz.) angesehen werden. KX wäre dann nämlich weitgehend dissoziiert und die Zurückdrängung, der Dissoziation durch überschüssiges KCl sehr gering; obgleich die KCl-Konzentration der Membran sich mit c ändert, bliebedie Dissoziation von KX doch unbeeinflusst: C_X ist von C unabhängig.

Unter Berücksichtigung dieser Verhältnisse giebt die Gleichung V den charakteristischen Verlauf der b. P. D. gut wieder. Wir betrachten zunächst die Grenzbedingungen.

(1) Sehr kleine wässrige Konzentrationen.—Die Gültigkeit der Nernst'schen Formel in der einfachsten Form kommt bei sehr kleinem c; offenbar dadurch, dass K neben $\left(\frac{C_X}{2c}\right)^2$ vernachlässigt-werden kann. Gleichung V nimmt danndie Form an

$$\text{b.P.D.} = \frac{RT}{nF} \ln \frac{C_X}{c} + \text{const.}$$

$$\text{oder} = \frac{R\,T}{n\,F} \ln \frac{1}{c} + \text{const.}^1$$

d.h. die b. P. D. ändert mit c wie eine Elektroden-Potentialdifferenz.

(2) Sehr grosse wässrige Konzentrationen.—In diesem Falle kann umgekehrt $\left(\frac{C_X}{2c}\right)^2$ neben K vernachlässigt werden. Die Formel V nimmt die einfache Gestalt an

$$\text{b. P. D.} = \frac{RT}{nF} \ln \sqrt{K} + \text{const.}$$

d.h. bei hohen Konzentrationen ist die b.P.D. von c unabhängig.

Das experimentum crucis für die Brauchbarkeit unserer Theorie bieten jedoch *die mittleren Konzentrationen*, denn offenbar können die Grenzbedingungen auch durch eine einfache empirische Gleichung wie z. B.

$$\text{b.P.D.} = \frac{R\,T}{n\,F} \ln \left(\frac{1}{c} + K\right) + \text{const.}$$

zum Ausdruck gebracht werden. Die Art und Weise, mit der die b.P.D. vom Grenzwert bei hohen Konzentrationen absinkt, wenn die Lösung stufenweise verdünnt wird, muss experimentell mit den Forderungen der Theorie verglichen werden. Zwecks empirischer Prüfung der Gleichung V. müssen die Konstanten, C_X und K, zunächst empirisch bestimmt werden. Eine einzige Bestimmung ist wie die folgenden Ableitungen zeigen, hierfür genügend. Mathematisch am einfachsten ist es, als empirische Differenz diejenige bei $C = 1/500$ normal und der Grenz E.M.K. bei sehr grossem c zu wählen. Es gilt dann bei Zimmertemperatur

$$\text{E.M.K.}_{\text{bei } c=1/500} = 0.058 \text{ lg } (250\ C_X + \sqrt{250^2 C_X{}^2 + K}) = \text{const.}$$

$$\text{E.M.K.}_{\text{limit}} = 0.058 \text{ lg } \sqrt{K} + \text{const.}$$

Differenz: $\text{E.M.K.}_c = {}_{1/500} - \text{E.M.K.}_{\text{limit}} =$

$$0.058 \text{ lg } \frac{250 C_X + \sqrt{250^2 C_{X^2} + K}}{\sqrt{K}}$$

Diese Differenz setzen wir gleich 0.058 lg 1/m, wo m also eine experimentell zu bestimmende Grösse ist.

Es folgt

$$250\, C_X + \sqrt{250^2 C_X{}^2 + K} = \frac{1}{m} \sqrt{K}$$

Auflösung dieser Gleichung nach $\sqrt{K}$:

$$\sqrt{250^2 C_X{}^2 + K} = \frac{1}{m} \sqrt{K} - 250 C_X$$

quadriert: $$+K = \frac{1}{m^2} K - 500\ \frac{1}{m} \sqrt{K}\, C$$

mit $\sqrt{K}$ dividiert: $$\sqrt{K} = \frac{1}{m^2} \sqrt{K} - 500 \frac{1}{m} C_X$$

$$-\sqrt{K}+\frac{1}{m^2}\sqrt{K}=500\frac{1}{m}C_X$$

$$\sqrt{K}=\frac{500\ C_X}{m\left(\frac{1}{m^2}-1\right)}$$

Berücksichtigt man, dass lg 1/m gewöhnlich etwagleich 2 ist, $\frac{1}{m^2}$ also circa 10000, so kann statt $\frac{1}{m^2}-1$ geschrieben werden $\frac{1}{m_2}$. Für $\sqrt{K}$ ergiebt sich dann näherungsweise

$$\sqrt{K}=500\ m\ C_X.$$

Dieser Wert in V substituiert giebt für

$$\text{b. P. D.}=\frac{RT}{nF}\ln\left(\frac{C_X}{2c}+\sqrt{\frac{C_X{}^2}{4c^2}+500^2{}_m{}^2C_X{}^2}\right)+\text{const.}$$

Die Differenz zweier beliebigen E.M.KK., die sich nur durch die Konzentrationen c_1 resp. c_2 an der Grenze der Membran unterscheiden, ist also

$$E_{c1}-E_{c2}=0.058\log\frac{\frac{C_X}{2_{c1}}+\sqrt{\frac{C_X{}^2}{4_c{}^2}+500^2{}_m{}^2C_X{}^2}}{\frac{C_X}{2_{c2}}+\sqrt{\frac{C_X{}^2}{4_c{}^2{}_2}+500^2{}_m{}^2C_X{}^2}}$$

Wie man sieht hebt sich C_X aus dem Quotient hinter dem log heraus; wird der Quotient ausserdem mit 2 erweitert, so ergiebt sich:

$$E_{c1}-E_{c2}=0.058\log\frac{\frac{1}{c_1}+\sqrt{\frac{1}{c_1{}^2}+1000^2{}_m{}^2}}{\frac{1}{c_2}+\sqrt{\frac{1_2}{c_2}+1000^2{}_m{}^2}}$$

$$=0.058\log\frac{\frac{1}{c_1}.\left(1+\sqrt{1+10^6{}_{m2c1}{}^2}\right)}{\frac{1}{c_2.}.\left(1+\sqrt{1+10^6{}_m{}^2{}_{c2}{}^2}\right)}$$

$$E_{c1} - E_{c2} = 0.058 \log \frac{c_2}{c_1} - 0.058 \log \frac{1 + \sqrt{1 + 10^6{}_m{}^2 C_2^2}}{1 + \sqrt{1 + 10^6{}_m{}^2 C_1^2}}$$

m war oben definiert durch die Beziehung

$$\log \frac{1}{m} = \frac{E_{c=\frac{1}{500}} - E_{\text{limit}}}{0.058}$$

EXPERIMENTELLE PRÜFUNG DER THEORIE

Diese Formel gilt, wenn KCl als Elektrolyt zugegen ist oder auch bei irgend einem anderen binären einwertigen Elektrolyten; für zwei wertige Elektrolyte wie $CaCl_2$ lässt die Theorie eine kompliziertere Beziehung voraussehen. Die experimentelle Prüfung geschieht durch Messung der E.M.K. von Ketten wie.

Kalomel Elektrode	Apfel oder Blatt	Lsöaung vriabler Zusammensetzung	Kalomel Elektrode
		a	b

In dieser Kette ist ausser der b.P.D. bei *a* durch dasDiffusionspotential bei *b* von der Konzentration der variablen Lösung abhängig. Bei *KCl* als *Elektrolyt* in der variablen Lösung sowie in der Kalomelelektrode (konstant 1/10 n) kann das Diffusionspotential bei *b* als unveränderlich angesehen werden, und es sind deshalb solche Versuche zur Prüfung der Theorie besonders geeignet.

1. Versuchsreihe beim Apfel (KCl als Elektrolyt)

Gemessen bei $c = \frac{1}{500}$ n KCl: 0.0874 Volt

Gemessen bei $c = \frac{1}{n}$ oder $\frac{1}{2}$ n KCl: —0.0220 Volt Dies kann als dem Grenzwert der b.P.D. entsprechend angesehen werden.

$$\text{Es ist somit } \log \frac{1}{m} = \frac{0.1094}{0.058} = 1.8862$$

$$\lg\ m^2 = -3.7724$$

$$10^6\, m^2 = 217.6$$

$$Ec_2 - Ec_1 = 58 \lg \frac{c_2}{c_1} - 58 \lg \frac{1 + \sqrt{1 + 21F_6C_2^2}}{1 + \sqrt{1 + 21F_6C_1^2}}$$

(in Milli Volt)

Kohzentrations-Intervall	Berechnet (Milli Volt)	Beobachtet bei zunehmender	abnehmender Konzentration	Mittel
1/1 bis 1/2	1.5		1	1
1/2 bis 1/4	3.0	6.7	3.0	4.9
1/4 bis 1/8	6.0	9.6	6.0	7.8
1/8 bis 1/16	10.5	8.9	11.3	10.1
1/10 bis 1/20	12.0	13.2	12.8	13.0
1/20 bis 1/40	15.0	15.6	12.8	14.4
1/40 bis 1/80	17.0	16.0	14.7	15.3
1/2 bis 1/40	12.6	19.0	21.0	20.0
1/4 bis 1/20	21.0	15.5	26.5	21.0
1/8 bis 1/40	30.0	32.0	30.0	31.0
1/16 bis 1/80	36.6	38.6	35.0	36.8

Wie man sieht, sind bei Anderung der Konzentration in entgegengesetzter Richtung die Anderungen der E.M.K. nicht völlig gleich, besonders bei hohen Konzentrationen besteht diese Unsicherheit. Angesichts dieser mangelhaften Reversibilität kann die Ubereinstimmung mit der Theorie als befriedigend angesehen werden, die Abweichungen der beobachteten Mittelwerte von den berechneten sind nur in einem Falle grösser als 2 Milli Volt (Intervall 1/2 bis 1/40), in den übrigen zehn Fällen kleiner. Eine grössere Genauigkeit als 2 Milli Volt kann bei solchen Messungen nicht erzielt werden. (Die Messung geschah n. b. mit einem empfindlichen Spiegelelektrometer.)

Eine weitere Versuchsreihe wurde ebenfalls am Apfel mit KCl ausgeführt, wobei die Konzentrationsintervalle andere waren.

Gemessen bei $c=\frac{1}{500}$ KCl 0.0750 Volt

Gemessen bei $c=\frac{1}{1}$ KCl -0.0294 Volt

Es ist somit $\lg\frac{1}{m}=\frac{0.1046}{0.058}=1.8034$

$10^6 m^2=247.28$

Konzentrations-Intervall	Berechnet (Milli Volt)	Beobachtet
1/500 n bis 1/250 n	17.5	17
1/250 n bis 1/125 n	17.0	15.2
1/125 n bis 1/25 n	38.5	36.3
1/50 n bis 1/25 n	16	16
1/25 n bis 1/5 n	23.5	27
1/5 n bis 1/1 n	6.5	8
1/1 n bis 2 1/2 n	1	1 in entgegengesetzter Richtung

Auch bei diesen Versuchen ist die Ubereinstimmung befriedigend.

Messungen der gleichen Art wie die eben beschriebenen mit dem *Blatt einer Gummipflanze* (ficus elastica) sind in der genannten früheren Arbeit gegeben. Ich möchte auch für diese Messungen die hier abgeleitete Formel prüfen.

Konzentrations-Intervall	Beobachtet (Milli Volt) I	II	III	Mittel	Berechnet
1/1250 bis 1/250	31	33	35	33	40
1/250 bis 1/50	30	32	31	31	36.5
1/50 bis 1/10	23	31	21	23	18.5

Zur Ausführung der Berechnung war Kenntnis des Grenzwertes der Kraft, welcher bei noch höherer Konzentration erreicht wird erforderlich. Es wurde in besonderen Versuchen gefunden

Konzentrations-Intervall		Die Berechnung ergab
1/10 n bis 1/2 n	Milli-Volt	Milli-Volt
1/2 n bis 5/2 n	Milli-Volt	Milli-Volt

Was die Berechnung für diese Beispiele betrifft, so wurde hier soverfahren, dass die Grösse m definiert wurde durch die Beziehung

$$\log \frac{1}{m} = \frac{E_{C=\frac{1}{250}} - E_{\text{limit}}\ (2\tfrac{1}{2}n)}{0.058}$$

Entsprechend lautet die Hauptformel:

$$E_{C_2} - E_{C_1} = 58 \log \frac{C_2}{C_1} - 58 \log \frac{1+\sqrt{1+500^2m^2C_2^2}}{1+\sqrt{1+500^2m^2C_1^2}}$$

(Milli Volt)

In derselben Weise möchte ich auch Versuche mit NaCl-Lösungen verschiedener Konzentration, welche sich in der früheren

Arbeit angegeben sind durchgerechnen. Bei diesen Experimenten ist jedoch zu beachten, dass in der entsprechenden Kette

Kalomel Elektrode	Blatt des Gummibaums	NaCl-Lösung wechselnder Konzentration	Kalomel Elektrode
	a	b	

auch das Diffusionspotential bei *b* sich mit der Konzentration der variablen Lösung andert. (Die Kalomelelektroden waren bei diesen Versuchen mit 1/10 n NaCl-Lösung gefüllt.) Nach einer bekannten Formel kann für Verfünffachung der Konzentration die Anderung des Diffusionspotentials gleich $\frac{u-v}{u+v} \cdot 0.058 \cdot \lg 5$ gesetzt werden, diese Grösse kann für NaCl-Lösungen nicht so wie bei KCl vernachlässigt werden, da u und v nicht völlig gleich sind, es ergiebt sich vielmehr hierfür der Wert 0.008 Volt. Diese Anderung ist in dem Sinn, dass die variable Lösung mit steigender Verdünnung negativer gegen die Kalomelelektrode wird (da das negative Ion Cl eine grosser Wanderungsgeschwindigkeit als das positive Na hat). Somit ist die Anderung in dem gleichen Sinne wie die Gesamtwirkung der Konzentrationsänderung: bei Verdünnung wird die rechte Seite der obigen Kette positiver, und es ist von der gemessenen Gesamtdifferenz bei Verfünffachung der Konzentration 0.008 Volt abzuziehen, um die Differenz der b.P.D. zu erhalten.

Zur Berechnung möchte ich die zweite NaCl-Versuchsreihe, welche in der genannten Arbeit mitgeteilt ist, wählen, es war gefunden:

Konzentrations-Intervall	Differenz gefunden	Nach Abzug des Diff. Potentials	Berechnet
1/1250 bis 1/250	38	30	37.5
1/250 bis 1/50	36	28	37
1/50 bis 1/10	24	18	14.5

In einer anderen (nicht mitgeteilten) Versuchsreihe, für welche das Konzentrations-Intervall 1/50 bis 1/10 dieselbe Differenz der Kraft gab wie oben, ergab sich für

1/10 bis 1/2	13	5	3.5
1/2 bis 5/2	11	3	1.0

Für die Berechnung wurde in diesem Falle gesetzt

$$\log \frac{1}{m} = \frac{0.052}{0.058} = 0.8966$$

$$E_{C2} - E_{C1} = 58 \lg \frac{C_2}{C_1} - 58 \lg \frac{1 + \sqrt{1 + 500^2 m^2 C_1{}^2}}{1 - \sqrt{1 + 500^2 m^2 C^{12}}}$$

Die Uebereinstimmung mit den theoretischen Werten ist bei diesen letzten Versuchen weniger gut als bei den ersten. Ich glaube, das dadurch erklären zu können, dass diese letzten Versuchsreihen nicht an ein und demselben Objekt hintereinander durchgeführt wurden, somit von Unsicherheiten durch Verschiedenheit des biologischen Materials weniger frei sind. Die NaCl Versuche sind ausserdem mit den Unsicherheiten behaftet, die Berechnung von Diffusionspotentialen mit sich bringt.

Die hier abgeleiteten Formeln sind *nur bei binären Elektrolyten* gültig. Die Veränderlichkeit der b.P.D. gegen $CaCl_2$ oder $BaCl_2$, Lösungen worüber auch einige Versuche vorliegen, kann deshalb nicht in der gleichen Weise vorausberechnet werden. Die Theorie führt in diesem Falle auf Gleichungen dritten Grades, wodurch die mathematischen Ausdrücke alsbald eine sehr komplizierte Gestalt annehmen. Aus den vorliegenden Messungen scheint sich auch zu ergeben, dass der Gang der b.P.D. in diesem Falle etwas anders geartet ist, doch soll hierauf nicht näher eingegangen werden.

Zur richtigen Würdigung der vorliegenden Ergebnisse sei nochmals auf die Einzelannahmenhingewiesen, die zur Ableitung der Formeln nötig waren. Diese waren:

1. Gültigkeit des Verteilungssatzes (für Membran Lösung) in der einfachsten Form.
2. Ahnlichkeit der elektrolytischen Dissoziation in Membran und wässriger Lösung.
3. Unveränderlichkeit der Konzentration des Salzes KX (resp. NaX), welches den Elektrolyteigengehalt der Membran ausmacht von der äusseren wässrigen Konzentration. (d.h. vollständiger chemischer Umsatz in der Membran.)

Ohne diese Annahmen steigen die mathematischen Schwierigkeiten alsbald zum Unüberwundbaren, und es scheint mir dann eben unmöglich überhaupt zu quantitativen Beziehungen zu gelangen.

Man wird zugeben, dass diese Hilfsannahmenihrer Natur nach plausibel und in befriedigender Annäherung durch das Experiment bestätigt sind.

Ob und in wieweit sich bei Modification dieser Hilfsannahmen brauchbare Formeln ableiten lassen, soll späteren Untersuchungen vorbehalten werden.

BEZIEHUNGEN ZU NERNST'S THEORIE DER REIZUNG

In der früheren mehrfach erwähnten Arbeit, die der Verfasser mit Herrn Dr. J. Loeb ausgeführt, hat wurde bereits gezeigt, dass die Potentialdifferenzen an der Schnittfläche pflanzlicher Gewebe *qualitativ aber nicht quantitativ* sich ebenso verhalten wie solche an unverletzten Oberflächen: die Anderung der Potentialdifferenz mit der Konzentration der ableitenden Lösung erfolgt in demselben Sinne jedoch in erheblich kleinereren Beträgen. An der Hand der im Eingang dieser Arbeit gemachten Bemerkung, dass die Schnittfläche sich elektrisch wie ein Mosaik verhält, erscheint diese Beobachtung erklärlich. An der Grenze der durchschnittenen Membranteile wirkt die Konzentrations-Anderung wie an der unverletzten Rinde, an denjenigen Stellen jedoch, wo ableitende Lösung und Saft zusammenkommen, ist kein Einfluss der Konzentration auf die Potentialdifferenz vorhanden. Es sind also in diesen Versuchen gewissermassen zwei Ketten parallel geschaltet, solche mit wahren b.P.D. und solche mit Konzentrations-unabhängigen Diffusionspotentialen; der Gesammteffekt muss also offenbar eine kleinere Konzentrations-Veränderlichkeit als bei den b.P.D. sein, wie es auch tatsächlich beobachtet wird.

Möglich wäre es auch, die Erscheinungen an der Schnittfläche mit der Annahme zu deuten, dass die elektromotorisch wirksamen Membran mit einer fest anhaftenden wässrigen Phase bedeckt ist, die Konzentration der ableitenden Flüssigkeit kann sich dann nur durch Diffusion durch diese Schicht hindurch bemerkbar machen.

Tierische Gewebe der verschiedensten Art verhalten sich ähnlich den verletzten Pflanzenteilen, wie auch schon in der früheren Arbeit gezeigt wurde. Ich möchte an dieser Stelle noch einmal auf die interessanten Versuche von McDonald[1] und einen sich daraus

[1] Proc. Roy. Soc. *67*, 310 (1900).

ergebenden Zusammenhang mit der Nernst'schen Theorie der Reizung hinweisen.

McDonald hat analoge Versuche mit Warmblüternerven ausgeführt, wie sie von Herrn Dr. Loeb und mir mit Pflanzenteilen beschrieben wurden. Freilich ist hiermit weder die von uns erreichte Pracision zu konstatieren, und es konnte deshalb auch nicht die hier gegebene physikalische Erklärung gewonnen werden. Die wässrige Lösung, die an der äusseren Oberfläche des Nerven haftet, wird durch Einlegen in Lösungen verschiedener Konzentration in ihrer Konzentration geändert, und damit die E.M.K., die man bei Ableiten von Oberfläche und Querschnitt misst (gewöhnlich als Verletzungsstrom bezeichnet). Bekanntlich ist die Oberfläche positiv gegen den Querschnitt, und sie wird um so positiver je verdünnter die Spüllösung ist, in welche der Nerv gelegt war und welche also an der Oberfläche haftet. Also selbst bei diesen Objekten wirkt die Konzentration in dem gleichen Sinn auf die b. P. D. Ist es hiernach nicht berechtigt, die Beziehung zwischen b. P. D., wie sie oben entwickelt wurde, als charakteristisch für Membranen verschiedenster Art Anzusehen, wenigstens in gewisser Annäherung?

Mit zahlreichen elektro-physiologischen Erscheinungen müssen die b. P. D. offenbar in Zusammenhang stehen. Besonders interessant scheinen mir die Beziehungen zu der Nernst'schen *Theorie der Reizung*. Die unter diesem Titel gewöhnlich zusammengefassten Gesetzmässigkeiten beruhen auf einem so soliden Fundament von Tatsachen, dass die Bezeichnung Theorie kaum sehr treffend ist. Nernst[1] hat gezeigt, dass die Erregung eines und desselben Muskels unter dem Einfluss von oszillatorischen oder alternierendem Stromfluss bei wechselnden elektrischen Bedingungen immer dann eintritt, wenn der Stromfluss (oder die Entladung) eine gewisse maximale Konzentrationsveränderung an Phasengrenzen zu Stande bringen kann. Die Konzentrationsänderung an der Phasengrenze zweier Elektrolyte ist hierbei denselben Gesetzmässigkeiten wie an einer Metall Elektrode unterworfen, z. B. als Funktion der Stromstärke und Wechselzahl eines Wechselstromes, als: const. $\frac{i}{\sqrt{m}}$, wo i die Stromstärke, m die Periodenzahl des Wechselstroms bedeutet. In der Tat zeigt sich, dass für alle Wechselströme, welche gerade die Reizung eines und desselben Nerv-Muskelpräperates hervorrufen können, dieser Quotient konstant ist. Wie wir gesehen haben, bedingen Konzentrationsänderungen Anderungen der Potentialdifferenz. Hiernach scheint es bei der Reizung auf eine gewisse *maximale Polarisation* an der Grenzfläche Membran Lösung anzukommen. Dass diese Polarisation durch Vermittlung einer damit verknüpften Anderung der Oberflächenspannung in die Kette der Vorgänge eingreifen kann, soll hier nur angedeutet werden. Bemerkenswert ist, dass der Electrolytgehalt der meisten Körperflüssigkeiten konstant 1/8 molekular ist. Ein Blick auf die Tabelle auf Seite 44 zeigt, dass diese Konzentration für die b. P. D. insofern eine besondere Bedeutung hat, als Konzentrationssteigerung *nur mehr eine sehr kleine Anderung hervorbringen kann, Konzentrationserniedrigung dagegen eine sehr viel grössere.* Dies scheint mir nach dem oben erklärten Zusammenhang zwischen Polarisation und Reizung mit der Tatsache verknüpft zu sein, dass gleiche Stromstösse in verschiedener Richtung sehr verschiedene Reizeffekte haben. Bekanntlich ist die Reizung bei Schliessung eines Stromes sehr viel stärker an der Katode als an der Anode, bei Offnung umgekehrt. Die Konzentrations-Verschiebungen in entgegengesetzten Richtungen bringen eben sehr verschiedene Anderungen der b. P. D. hervor. Ubrigens würde dies auch der Fall sein, wenn für die b. P. D. eine einfache logarithmetische Konzentrationsabhängigkeit bestände, da der Stromstoss, die Absolutwerte der Konzentration nicht ihr Verhältnis ändert. Bei Gültigkeit meiner Formel ist die einseitige Wirkung der Konzentrationsänderung jedoch noch besonders ausgeprägt, und am meisten für *die* Salzkonzentrationen, welche in den Körpersäften vorkommen.

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[1] Proc. Roy. Soc. *67*, 310 (1900).

[2] Sitzungsber. d. preuss. Akad. 1908, I, 1. Siehe auch Pflüger's Archiv, 122, 307 (1908).

Eine andere Erscheinung, welche vielleicht in demselben Zusammenhange eine Erklärung ist, ist die folgende. Overton[3] erwähnt, dass die Reizbarkeit von Muskeln in hyperisotonischen Lösungen

[3] Pflüger's Archiv, *92*, 346.

(>1/8 mol) schneller verloren geht als in hypoisotonischen (<1/8 mol), obgleich in beiden Fällen schädigende Einflüsse sich bemerkbar machen. Die Tabelle auf Seite 44 zeigt, dass bei Konzentrationen, die wesentlich höher als 1/8 mol. sind, die b. P. D. sich nahezu in dem konzentrationsunabhängigen Gebiete befindet, es ist keine Polarisation möglich und damit der Erregungsvorgang gehemmt. Es soll indes nicht geleugnet werden, dass Konzentrationsänderung in diesen Fällen auch durch osmotische oder chemische Vorgänge Veränderungen im Gewebe hervorrufen kann, die ihrerseits die Reizbarkeit beeinflussen.

Höber nennt in seinem Buche ueber die physikalische Chemie der Zellen die konstante Körpertemperatur und den konstanten Salzgehalt des Blutes als die zwei auffallendsten allgemeinen Eigenschaften aller höheren Organismen. Für die Bedeutung der erhöhten Temperatur lässt sich eine Erklärung, wie er zeigt, geben, nicht aber für den konstanten Salzgehalt. Eine solche ist hier gelungen, meines Wissens zum ersten Male.

CONCLUSIONS

1. Potential differences at the junction of an uninjured part of a plant and an aqueous solution of an electrolyte vary with the concentration of the electrolyte, as Dr. Loeb and the writer have shown.

2. The following formula was derived representing the relation between variation of potential difference and concentration.

Pot. Diff. 1 — Pot. Diff. 2

$$= 0.058 \log. \frac{C_1}{C_2} - 0.058 \log \frac{1 + \sqrt{1 + 10^6 m^2 C_1^2}}{1 + \sqrt{1 + 10^6 m^2 C_2}}$$

where is given by the relation

$$\log. \frac{1}{m} = \frac{\text{limit of the pot. diff.} - \text{pot. diff. for } c = n/500}{0.058}$$

In the derivation of this formula the following assumptions were made: (a) that a complete reaction takes place between a constituent of the membrane and the aqueous electrolyte. In this reaction a salt is formed which is insoluble in water but distributed in the membrane homogeneously. (b) that the electrolyte as such is contained in the membrane in minimal concentration and that

in accordance with the law of partition the ratio of concentration of electrolyte in membrane and in water is constant.

3. The formula was tested experimentally by means of measurements on apples (table, page 44). As required by the formula at high concentrations the difference of potential approaches a limit; at low concentrations the potential difference follows a simple logarithmic relation; the formula is also valid for intermediate concentrations.

4. If we assume that variations in potential difference induce stimulation, it is possible from the results given above *and* with aid of *Nernst's theory of stimulation* to explain some electrophysiological observations; examples of which are (1) the different effect on stimulation of cathodical closing and of anodical closing; (2) the diminution of irritability in hypertonic salt solutions.

THE PRESENT STATUS OF THE TEMPERATURE SCALE

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The past few years have been marked by great advances in the exact determination of the temperature scale in terms of fixed points of melting, transformation, or boiling, of pure substances, extension of the scale both upwards and downwards, the correlation of the various physical phenomena and their mathematical expression in terms of which interpolations and extrapolations may be expressed, and in the invention and improvement of temperature measuring apparatus and methods.

The Thermodynamic Scale. The fundamental basis for the determination of the temperature scale is obtained by measurements with some form of gas thermometer. The accuracy with which these and auxiliary measurements may now be made, together with the great purity now obtainable of the materials suitable for standard points, and the state of our knowledge of the gas laws, permits the expression of temperatures in terms of the *thermodynamic* or ideal-gas scale, a scale which is independent of the properties of any particular substance and to which the usual gas scales approximate so closely that, for most purposes, it is not necessary to distinguish between them. The radiation laws, in terms of which extrapolation to the highest temperatures is made, are also based on the thermodynamic scale; so that, using this as our standard, we have a single temperature scale from the lowest to the highest temperatures. The corrections to apply to the scales given by gases, to reduce to the thermodynamic scale, are not yet known with all the certainty that may be desired especially at very low and very high temperatures, but in the former region the thermometric gases used, hydrogen and helium, depart less from the ideal state than any others, and in the case of helium the correction is practically negligible over almost the complete range of temperatures.

In the most recent researches in exact gas thermometery it is more and more the practice to reduce results to the thermodynamic scale, a practice that should become universal.

The Gas Scales. The only methods of temperature measurement that are directly reducible to the thermodynamic scale are those based on the gas thermometers at constant pressure and constant volume, by means of computations based on the known properties of these gases.

The following table (Table I) based on recent computations[1] represents well enough the corrections to the gas scales in ordinary use and over the ranges within which these gases may be used to advantage.

TABLE I. SCALE CORRECTIONS FOR GASES. $\theta_0 = 273°.10$ C.

Temperature Centigrade	Constant Pressure=76 cm.			Constant Volume, p_0=100 cm.		
	Helium	Hydrogen	Nitrogen	Helium	Hydrogen	Nitrogen
−250	......	......	......	+.02	......	......
−200	+.10	+.26	......	+.01	+.06	......
−100	+.03	+.03	+.33	.000	+.014	+.07
−50	+.009	+.004	+.09	.000	+.004	+.02
+25	−.002	−.002	−.013	.000	.000	−.006
+50	−.002	−.003	−.017	.000	.000	−.006
+75	−.002	−.002	−.012	.000	.000	−.004
+150	+.005	+.003	+.04	.000	+.001	+.01
+200	+.01	+.01	+.10	.000	+.002	+.04
+450	+.07	+.04	+.50	.00	+.01	+.15
+1000	+.24	+.01	+1.7	......	+.04	+.70
+1500	......	......	+3.0	......	......	+1.3

Within the fundamental interval, 0° to 100° C., the temperature scale has been defined by the International Committee on Weights and Measures in terms of hydrogen at constant volume under a pressure of 1000 mm. of mercury. This scale, as closely as it is known, appears to be practically identical with the thermodynamic scale. For lower temperatures the hydrogen and helium scales are used, the latter for the very lowest attainable, or to less than 1°2 K according to Kammerlingh Onnes. For high temperatures, especially above 450° C., nitrogen at constant pressure is usually used although there is not here, nor for the range below 0° C., any international agreement as to the temperature scale. The upper limit attained is the melting point of palladium, 1550° C. There is no necessity, at least from the point of view of the determination of temperatures, of extending gas thermometer measurements higher than this, as the thermodynamic scale is more nearly realized for those high regions by means of instruments based on the radiation laws the constants of which may be determined below 1550° C.

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[1] See in particular computations by:
Callendar, Phil. Mag. (6) *5*, 48, 1903.
D. Berthelot, Trav. et Mém. Bur. Int. *13*, 1903.
Buckingham, Bull. Bureau Standards *3*, 237, 1907.
Kammerlingh Onnes and Braak, Seiden Coms. 97b, 102b, 1907.
Rose Innes, Phil. Mag. (6) *2*, 130, 1901.

Secondary Methods and Scales. The most commonly used secondary temperature measuring instrument is the *mercury in glass thermometer*, the reductions of which to the hydrogen or thermodynamic scale, after all other corrections are made, depends on the kind of glass of which it is made and to a much smaller extent on the history of the thermometer. The normal hydrogen scale is preserved at the International Bureau by means of four *verre dur* thermometers.

For high temperature thermometers — from 300° to 520° C. or more — the mercury is confined under pressure exerted by an inert gas; and if quartz is substituted for glass, 750° C. may be reached with mercury. For low temperatures the mercury may be replaced by toluene to −90°, and by pentane to liquid air temperatures.

All thermometers of the above types have to be calibrated empirically and individually in terms of known standards of temperature.

The Platinum Resistance Thermometer over the range in which it remains constant and sensitive, from −200° C. to +1000° C., and when properly designed, constructed and used, is the most exact secondary instrument we have, and has been of great service recently in coördinating and comparing the gas thermometer observations on basal temperatures of several recent observers.[1] For example, the lower freezing-point values, cadmium, zinc, etc., of Day and Sosman,[1] as well as boiling points of naphthalene and benzophenone by Jaquerod and Wassmer,[2] were shown definitely by the resistance thermometer measurements of Waidner and Burgess[3] to be incompatible with the most probable value of the sulphur boiling point (=S.B.P.), one of the most important of the base points, as it is commonly used with the freezing and boiling points of water, as the third calibration point of platinum resistance thermometers. The latest work on the sulphur boiling point[4] with the constant volume gas thermometer has reduced the uncertainty of this temperature, which we may take as 444.6 on the thermodynamic scale, to less than 0°.1 C., whereas a year ago this uncertainty was nearly 1°.0 C.

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[1] Holborn and Henning, Ann. d. Phys. *35*, 761, 1911.
Waidner and Burgess, Bull. Bureau Standards *6*, 149, 1910; *7*, 1, 1910.
Dickinson and Mueller, Jl. Wash. Acad. Sci. *2*, 176, 1912.

The usual Callendar, or difference formula for reducing platinum temperatures, $pt=100\ (R-R^0)\ /(R^{100}-R^0)$, to true temperatures, namely: $t-pt=\delta(t/100-1)\ t/100$, where δ is a function of the purity of the platinum, has been shown recently[5] to be of more general and exact application over a wider range of temperature than had hitherto been supposed. Using a base point within the fundamental interval such as the transformation point of sodium sulphate, 32°.383[6] as the third calibration temperature, the value of δ for pure platinum is 1.47_0 to 1.48_0, and using the S.B.P., 444.6, the value of δ is 1.48_4 to 1.49_4. In other words, calibrating a platinum resistance thermometer in ice, steam and sulphur vapor will give the normal International Hydrogen Scale, within the fundamental interval, 0° to 100°, to 0.004° C. or to closer than the International Bureau can reproduce its scale with certainty. In this range the platinum thermometer is reliable to better than 0°.001 C. Using the platinum thermometer at high temperatures,

[1] Day and Sosman, Am. Jl. Sci. *29*, 93, 1910. Reprint 157, Carnegie Institution of Washington, 1911.

[2] Jaquerod and Wassmer, Jl. Chim. Phys. *2*, 52, 1904.

[3] Waidner and Burgess, l. c.

[4] Holborn and Henning, l. c.
Day and Sosman, Am. Jl. Sci. *33*, 517, 1912. Jl. Wash. Acad. Sci. *2*, 167, 1912.

[5] Adams and Johnston, Am. Jl. Sci. *33*, 534, 1912. Jl. Wash. Acad. Sci. *2*, 275, 1912.
Holborn and Henning, l. c.
Dickinson and Mueller, l. c.
Waidner and Burgess, l. c.

[6] Richards and Wells, Zs. Phys. Chem. *43*, 465, 1903.
Dickinson and Mueller, Bull. Bureau Standards, *3*, 641, 1907.

or to 1100° C., in the same way with the Callendar formula, the temperature scale is reproduced as closely as this scale has been located by gas thermometer measurements, or to within 2° at 1100° C. It has been suggested to write the δ in the form $\delta = \delta + a\,t$. There appears to be no certain advantage of this more complex expression, however, for pure platinum.

For very low temperatures the Callendar formula breaks down, but to −200° C. it may be used with considerable exactness if the boiling point of oxygen −182.9, or the sublimation point of carbonic acid, −78°.34, is taken as the third calibration temperature. Complex exponential functions have also been suggested for very low temperatures, and resistances expressed in powers of temperature even to the fifth are sometimes used.

In precision calorimetry, the platinum thermometer replaces that of mercury to advantage, for when properly constructed the former has no appreciable zero change or hysterisis with use and time if not exposed to high temperatures, and it is as easy to measure small temperature differences at 25° C. to 0°.0001 C. with the platinum as to 0°.001 with the mercury thermometer. A great and unique practical advantage of the former for all uses above −100° C. is the fact that its calibration is made and controlled by only three fixed points which are easily realized with exactness, two of which are the ice and steam points and the third *any* other known temperature which is most convenient.

The platinum thermometer becomes, therefore, the most satisfactory secondary standard for the calibration of all other types of thermometers between −200 and +1100° C. In fact, if the International Bureau were destroyed and all the existing copies of its thermometer standards as well, the International scale would be perpetuated with entire satisfaction by means of the platinum thermometer which may be constructed and calibrated independently anywhere it may be desired.

The Thermoelectric Thermometer, in general, is not an instrument of such great precision nor of such simple calibration as the platinum resistance thermometer, a formula involving three and even four or more powers of temperature in terms of E.M.F. being required for all thermocouples used with the highest accuracy over several hundred degrees and at low temperatures over very much shorter ranges.[1]

For temperatures below −200° C. a thermocouple of gold-silver[2] appears to best meet the requirements of a secondary instrument. For ordinary temperatures satisfactory couples are those of iron-constantan and copper-constantan; for high temperatures the LeChatelier couple of Pt, 90 Pt-10 Rh.

For a moderate precision, the thermocouple is a most convenient instrument and the calibration may then be reduced to three or even two reference temperatures. In the last case, for the Pt-Rh couple, the best formula appears to be Holman's, $\log e = a + b \log t$, for which, if the zinc and copper freezing points are used as calibrating temperatures, the scale is off by less than 2°.5 between 200 and 1300° C. and by less than 5° to the melting point of platinum. For no form of thermocouple does it appear that the inverse function, which is the more convenient to work with, namely, $t = a + be + c\,e^2 + d\,e^3 + \ldots$, represents the temperature scale with the same exactness as the form $e = a + bt + ct^2 + dt^3 + \ldots$ with a like number of terms.

In the following table (Table II) are given the corrections to the readings of Pt, 90 Pt-10 Rh thermocouples calibrated at the freezing points of zinc, antimony and copper (see Table III) for the usual three-term formula and in zinc and copper for the formula of two terms. The couples of Pt, 90 Pt-10 Ir have nearly the same corrections.

TABLE II. CORRECTIONS TO THERMOCOUPLE SCALES
(PT, 90 PT-10 RH.)

Formula t=	300	600	900	1200	1400	1600	1700	1750
$e = a + bt + ct^2$	−0.8	0	+0.3	+0.5	+8	+26	+40	+46
$\log e = a + bt$	−0.6	+1.5	+2.5	−5	−5	−3	+1	+3

[1] Day and Sosman, l. c., and Sosman, Am. Jl. Sci. *30*, 1, 1910. Platinum rhodium at high temperatures.
Dickinson, Mueller and White: Copper constantan between 0−100. Phys. Rev. *31*, 159, 1910.
Adams and Johnston: Cu—Cn between 0 and 300, l. c.
J. Clay: Couples at very low temperatures. Leiden Coms. 107d, 1908.

[2] J. Clay, l. c.

The inherent weakness, as compared with the platinum resistance thermometer, of any thermocouple as a secondary temperature standard is the impossibility of eliminating in the measurements the E.M.F. effects along the whole length of the wires between hot and cold junctions of the thermocouple, and no wire yet examined appears to be completely free from such effects of inhomogeneity.

For the estimation of very high temperatures we have the *radiation laws of Wien and of Stefan,* preference being given to the former based on the use of monochromatic light, mainly on account of experimental convenience, although the theoretical foundation of the second based on the use of total radiation is the more certain. The characteristic constants of neither of these laws are as yet determined in a wholly satisfactory manner, although considerable has been done in recent years on this subject, and work is still in progress.

We may take the value 14,500 for the characteristic constant c_2 in Wien's law $\log I/I_1 = c_2\lambda \log e \ (1/T_1 - I/T,)$ in which I is the intensity of light of wave-length λ at an absolute temperature T. The recent determinations of c_2 all lie between 14,200 and 14,600. For the constant σ of Stefan's law connecting total radiation and temperature, $E = \sigma \ (T^4 - T_o{}^4)$, the value $\sigma = 5.80$ watt. cm.^{-2} deg.^{-4} appears to be the most probable, although the range of recent determinations is 5.30 to 6.51.

Standard Temperatures. Limiting ourselves to determinations made since the year 1900, and selecting only temperatures in the location of which two or more independent observers have participated, and which are suitable to use as check points in physical and chemical operations, the following temperatures (Table III) may be used as standard. They are given in terms of the thermodynamic scale, and for above 1550° C., the constant c_2 of Wien's law is taken as 14,500. Boiling points are for a pressure of 760 mm. Hg, and are given only for substances that do not attack platinum and for which it has been shown they remain constant over long periods of boiling.

TABLE III. STANDARD TEMPERATURES. THERMODYNAMIC SCALE

Substance	Phenomenon	Temperature C	Uncertainty C°	Repr'ducibility C°
Hydrogen	Boiling	−252.7	0.2	0.05
Oxygen	Boiling	−182.9	0.1	0.03
Carbon dioxide	Sublimation in gasolene	−78.34	0.1	0.03
Mercury	Freezing	−37.7	0.1	0.05
Water	Freezing	0	0	0.001
$Na_2SO^4+10H^2O$	Transformation to anhydrous salt	32.383	0.002	0.001
Water	Boiling	100	0	
Naphthalene	Boiling	271.96	0.02	0.01
Tin	Freezing	231.85	0.1	0.05
Benzophenone	Boiling	305.90	0.05	0.02
Cadmium	Freezing	320.92	0.1	0.03
Lead	Freezing	327.4	0.1	0.05
Zinc	Freezing	491.4	0.1	0.15
Sulphur	Boiling	444.6	0.1	0.03
Antimony	Freezing	630.	0.5	0.3
Ag^3-Cu^2	Eutectic freezing	779	1.0	1.0
NaCl	Freezing	800	2.0	1.0
Silver	Freezing	960.5	1.0	0.5
Gold	Freezing	1063	2.0	1.0
Copper	Freezing	1083	2.0	1.0
Palladium	Freezing	1549	10	3
Platinum	Melting	1755	15	5
Alumina	Melting	2000	30	20
Tungsten	Melting	3000	100	25
Carbon arc	Pos. crater	3600	150	50
Sun	Surface	6000	500	100

For the temperatures dependent on atmospheric pressures we have:

Oxygen B.P.	$T=T_{760}+0.013\ (p-760)$
Carbon dioxide S.P.	$T=T_{760}+0.017\ (p-760)$
Water B.P.	$T=T_{760}+0.037\ (p-760)$
Napthalene B.P.	$T=T_{760}+0.058\ (p-760)$
BenzophenoneB.P.	$T=T_{760}+0.063\ (p-760)$
Sulphur B.P.	$T=T_{760}+0.0912\ (p-760)-0.000042\ (p-760)^2$

As to the chemical purity of the various substances, Mylius has shown[1] that the following metals may easily be had to 0.01 per cent or better: Au, Ag, Pt, Hg, Cu, Sn, Pb, Cd, Zn. Of the boiling substances, benzophenone and oxygen are the only ones to the purity of which special attention need be given. Due perhaps to the general practice of investigators working at very low temperatures to use the gas thermometer itself, instead of an auxiliary method, for measuring those temperatures, there is a dearth of exactly known fixed points in this part of the scale.

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[1] F. Mylius, Zs. Anorg. Ch. *74*, 407, 1912.

Examples of Standard Temperatures. Some of the standard temperatures, owing to their great importance, have been determined many times and are therefore particularly valuable as primary reference points. The actual status of our knowledge of the temperature scale is perhaps best illustrated by giving in detail the measurements since 1900 on some of the most carefully studied of these temperatures, such as the boiling points of oxygen and sulphur and the melting points of cadmium, gold, platinum, and tungsten.

OXYGEN BOILING POINT = *−182.9*

DATE	OBSERVER	METHOD	TEMPERATURE	
			Observed	Thermodynamic
1901	Holborn	H^2 scale const. vol.	+182.7	
1901	Dewar	H^2 scale const. vol.	−182.5	
1906	Grummach	Pentane therm.	-182.6_6	
1906	Travers, Jaquerod and Senter	H^2 scale const. vol. He scale const. vol.	-182.9_3 −182.8	-182.8_7
1908	Kammerlingh Onnes and Braak	H^2 scale const. vol.	-183.0_4	-182.9_9

SULPHUR BOILING POINT = *444.6*

1902	Chappuis and Harker	N^2 scale const. vol.	444.7[1]	444.8
1908	Eumorfopoulos	Air scale, const. press.	444.5_5[2]	444.9_3
1911	Holborn and Henning	H^2, He const. vol. N const. vol.	444.5_1[1] 444.3_9	444.5_1
1912	Day and Sosman	N^2 scale const. vol.	444.4_5[2]	444.5_5
1912	Dickinson and Mueller	(Day and Sosman's therm.)	444.2_8[1]	444.3^8

[1] Transferred by platinum resistance thermometer.
[2] Thermometer bulb in S vapor.

CADMIUM MELTING POINT = *320.9₂*

Date	Observer	Method	Temperature	
			Observed	Thermody'mic
1900	Holborn and Day	N^2 scale const. vol.[1]	321.7	321.8
1902	Kurnakow and Puschin	Thermocouple interpolation	321.0	
1904	Day and Allen	Thermocouple interpolation	321.7	
1909	Waidner and Burgess	Pt. resis. (S.B.P. = 444.60)[2]	320.9_4	320.9_4
1910	Day and Sosman	Thermocouple extrapolation[1]	320.0	320.1
1911	Holborn and Henning	H_2, He, N_2 scales const. vol.[2]	320.9_2	320.9_2
1912	Day and Sosman	Corrected from 1910 value[1]	320.8	320.9
1912	Adams and Johnston	Cu-Cn thermocouple interpolation	320.9_2	320.9_2

GOLD MELTING POINT[3] = *1063*[4]

1900	Holborn and Day	N^2 scale const. vol.	1064.0	1064.3
1902	D. Berthelot	Air-optical const. press.	1064	1065.6
1904	Jaquerod and Perrot	Air, CO, N^2, O^2 const. vol.	1067.2	1067.4
1908	Day and Clement	N^2 scale const. vol.	1059.3[5]	1059.5
1910	Day and Sosman	N^2 scale const. vol.	1062.4	1062.6

PLATINUM MELTING POINT = *1755* (BASIS: C_2 = 14,500)

Date	Authors	Method	Temperature
1903	Nernst	Total light from black body	1782
1905	Holborn and Henning	Combined optical and thermo-electric	1729
1905	Harker	Thermoelectric	1710
1906	Nernst and Wartenberg	Optical: Wien's law	1753
1907	Holborn and Valentiner	Optical: Wien's law	1760
1907	Waidner and Burgess	Optical: Wien's law	1753
		Radiation from Pt, 3 colors	1750
		Therm'lectric: various formulæ	1697–1757
1909	Féry	Radiation from Pt oxidizing at	1690
		Radiation from Pt reducing at	1740
1910	Sosman	Thermoelectric extrap. from Pd = 1549	1752
1910	Ruff	Optical about	1750

[1] Transferred by Pt-Rh thermocouples.

[2] Transferred by platinum resistance thermometer.

[3] All measurements were made by transfer with Pt-Rh thermocouples.

[4] Several determinations of the copper melting point (1083) have also been made and auxiliary methods have shown Cu − Au = 20° so that the gold point is better known than the table would indicate.

[5] Sample shown to contain iron from crucible.

TUNGSTEN MELTING POINT = *3000* (BASIS: $C_2 = 14{,}500$)

1906	Waidner and Burgess	Wien's law, lamp filament	32.00
1907-10	Waidner and Burgess	Wien's law, lamp filament	3080–3050
1907	Wartenberg	Wien's law, Wenhelt discharge	2930
1910	Pirani	Wien's law, lamp filament	3226
1910	Ruff and Goecke	Wien's law, in vacuum furnace	2597
1911	Forsythe	Wien's law, with wedge with vacuum furnace	2974 3030
1911	Pirani and Meyer	Wien's law with filament and strip	2997
1911	Langmuir	Total photometric	3177

International Temperatures. It is evidently of the greatest importance for chemists and others who have to express or locate many of their results in terms of temperatures, that they be able to do so in terms of a common scale, as otherwise confusion reigns when endeavoring to compare the numerical values assigned by different observers to the various phenomena.

For the past twenty-five years, thanks to the International Bureau of Weights and Measures, it has been possible to express results to 0°.002 C. within the fundamental interval 0° to 100° C., but outside this interval chaos has reigned.

Both at low temperatures and high, there have been almost as many scales as observers, and some of the outstanding differences were relatively very large, even within the past year, for example, 1° at the sulphur boiling point and 7° at the gold melting point.

The recent series of investigations mentioned above have rendered it possible, however, to greatly reduce the uncertainties, and the state of the art of temperature measurements is now such that it should not be difficult for the various standardizing laboratories to agree upon a common temperature scale which would be defined in some such manner as outlined above. In pursuance of this idea, the several national laboratories and the International Bureau are at present interchanging communications relative to the establishment by agreement of some such single temperature scale, and it is to be hoped that the outcome of these interchanges will be of great practical benefit and convenience for the certification and use of temperature-measuring instruments, and that thenceforth 500° C. or 1000° C., for example, will each convey but one idea of temperature as do 0° or 100° C. at the present time.

SUR LES THEORIES ET LES FORMULES DE LA CHIMIE-PHYSIQUE

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1.— *Les Théories*

A coté de l'admirable loi des phases de Gibbs,[1] la Chimie-Physique présente un ensemble de résultats véritablement illusoires. Déja, en 1901, M. Kahlenberg[2] et ses élèves, par des expériences précises et nombreuses, ont prouvé que la théorie de la dissociation électrolytique n'explique pas les phénomènes présentés par les solutions aqueuses.

En 1904, ayant étudié ces questions dans le but de vérifier des résultats suggérés par les expériences de Blondlot sur les rayons N, je suis arrivé aux mêmes conclusions que M. Kahlenberg,[3] et j'aimontré:

1o. Que l'action des bases dissoutes K.OH ou $Ba(OH)^2$ sur les sulfates métalliques est différente suivant que l'onver se la base dans le sel dissous, ou le sel dans la base;

2o. Que le pouvoir cryoscopique moléculaire des sulfates chromiques est en rapport avec l'hydrolyse de ces sels, mais qu'il est indépendant de leur degré d'ionisation.

Sans doute, l'hydrolyse ne suffit pas à expliquer les phénomènes de dissolution, et M. Arrhénius a été très bien inspiré en affirmant la nécessité d'un autre dédoublement de la particule dissoute. De l'hypothèse de Van't Hoff, touchant l'état moléculaire de la particule dissoute, M. Arrhénius a déduit le dédoublement en ions des sels et des acides minéraux dissous. Il confirmait ainsi l'idée de Williamson et de Clausius que la conductibilité des solutions nécessite la préexistence des ions dans les solutions conductrices. L'hypothèse Willamson-Clausius qui a donné un si grand poids à l'interprétation de M. Arrhénius, ne s'accorde peut être pas aussi bien avec les faits que celle de Sir Ol. Lodge. D'après ce savant, la séparation en ions ne préexiste pas; elle ne se fait qu'au moment du passage du courant.

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[1] Bancroft. Che Phase rule.

[2] L. Kahlenberg. The Theory of electrolytic dissociation,Bul. of the Univers. of Wisconsin, fev. 1901. Physic-Chemistry, 1901.

[3] C'est l'occasion de rappeler que ce grand savant a maintefois photographié les phénomènes d'extinction qu'il a signalés, et qu'il n'a jamais approuvé les exágérations publiées sur ce sujet, dont on n'est pas encore maitre des causes.

Dans la première hypothèse, la conductibilité d'une solution saline, déterminée par le nombre des ions préexistants, serait invariable à température fixe. Dans l'hypothèse de Sir Ol. Lodge, il se pourrait que des perturbations dans la conductibilité des sels, se fissent sous l'action du courant quand plusieurs modes d'ionisation sont possibles.

Voici quelques expériences qui me paraissent confirmer cette opinion. Elles sont relatives à la résistivité d'une solution de sulfate chromique violet à 2/10 Molécule par litre (Analyse: $Cr^2O^3 = 0{,}315$, $SO^4Ba = 1{,}417$). La détermination à 0°, de la résistance X de la solution par rapport à une résistance totale R à été obtenue à l'aide de l'appareil téléphonique de Dongier-Lesage, par l'équation suivante:

$$\frac{X}{R} = \frac{a}{1000 - a}$$

dans la quelle a représente la longueur de lar ègle qui correspond à l'extinction du téléphone. Généralement la valeur de a se détermine très nettement et très exactement.[1]

Cependant, dans les solutions chromiques qui nous occupent, varie à la longue. Voici les nombres observés de minute en minute à 0°, sur une solution de 24 heures:

$R = 23{,}08$ $a = 384$; 386; 387; 387;
$R = 13{,}08$ $a = 525$; 526; 527; 529; 530.

Une solution à 1/10 Molécule par litre donne:

$R = 23{,}08$ $a = 506$; 509; 510; 510.

La même solution abandonnée pendant 48 heures à la température ambiante, s'hydrolyse légèrement et donne à 0:

$R = 23{,}08$ $a = 488$; 498; 501; 504; 506; 507.

Il semble qu'avec le temps, on retrouve le nombre précédent 510. Mais si on laisse circuler le courant, la valeur a retombe à

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[1] Bull. de la Soc. Chim. 1908 et 1911, T. 9, p. 576 et 862.

501 au bout d'une minute, à 499 au bout de deux minutes, à 497 au bout de trois minutes.

Si de nouveau, on arrête le courant, on observe
ave R = 23,08, au bout de 2 minutes: $a = 504$,
au bout de 3 minutes: $a = 506$,
au bout de 7 minutes: $a = 509$,
au bout de 12 minutes: $a = 511$.

Le courant ayant été rétabli pendant une minute, on retombe à 505,5 et à 505 au bout de 2 minutes.

Après une nouvelle suppression de courant pendant 2 minutes on trouve: $a = 512$,
après suppression pendant 4 minutes, on trouve $a = 515$,
après suppression pendant 6 minutes, on trouve $a = 516$,
après suppression pendant 7 minutes, on trouve $a = 516$.

Un nouveau passage de courant pendant 1 minute redonne 507, puis 505 après 2 minutes. La valeur de a s'est élevée de 488 à 516.

La même liqueur deux fois plus étendue (c'est-à-dire au 1/100 Molécule) donne à 0° et de minute en minute:

Pour R = 93,08, $a = 596$; 597; 598; 600; 602.

Si on fait circuler le courant pendant 1 minute, on retombe à 599; si on l'arrête, on remonte à 602.

Les sulfates verts donnent des résultats analogues mais moins marqués.

On pourrait supposer que le passage prolongé du courant détermine un échauffement et diminue la résistance de la solution placée dans la glace. Je ne le crois cependant pas, car je n'ai rien constaté de semblable sur d'autres corps. En tout cas, chaque fois que la liqueur a été soumise à l'influence du courant, la conductibilité du sel refroidi change: a passant de 498 à 504 puis à 512.

Le courant parait donc agir sur le degré d'ionisation, loin d'être toujours réglé par cette condition. De sorte que la nécessité d'une ionisation préalable, indispensable au passage du courant, n'est plus une objection aux conclusions de M. Kahlenberg remémorées ci-dessus.

Déjà dans l'eau, M. Kahlenberg a signalé des molécules non dissociées qui sont conductrices. J'ai ensuite prouvé que la conductibilité des sulfates chromiques isomères n'a aucune relation avec leur degré d'ionisation. Dans certains solvants organiques, M. Kahlenberg et MM. Jones, Castoro....ont montré que la molécule reste normale et que néanmoins la conductibilité existe. MM. Walden, Werner, Lincoln, Dutoit....ont étendu ces observations à une dixaine de solvants.

Il résulte de ces faits que la conductibilité par ionisation des sels métalliques étant exceptionnelle, ne doit pas être érigée en règle.

L'HYPOTHESE DE VAN'T HOFF ET LA THERMODYNAMIQUE

Pour ces motifs et pour d'autres que je ne puis rappeler ici, puisque le Règlement du Congès s'y oppose, j'estime que le fondément de la Théorie des Ions, c'est-à-dire l'hypothèse de Van't Hoff elle même, est illusoire.

Discutons directement l'assimilation de la particule dissoute à la molécule gazeuse. Le fondement que lui a donné Van't Hoff n'a qu'une apparence de solidité. Il repose uniquement sur ce que la pression osmotique moléculaire π serait voisine de la pression moléculaire P qu'aurait le sucre s'il existait à l'état gazeux à la température ordinaire. De ce fait, il est en effet facile de conclure que $\pi.\ V=RT$ puisque P.V est égal à RT. Van't Hoff a préféré calculer R et conclure de $\pi V=RT$ l'égalité $\pi=P$.

1o. D'une part, il n'est pas certain que la molécule gazeuse du sucre soit $C^{12}H^{22}O^{11}=342$, à basse température. Autant admettre que la molécule du soufre est S^2 par analogie avec l'oxygène O^2.

Sans doute, si les expériences de Pfeffer, différant de 508 à 554, pour une même concentration, étaient peu faites pour admettre l'égalité $\pi=P$, celles de MM. Morse et Frazer ont donné depuis de milleurs résultats. Néanmoins, pour conclure que $R=847$, il ne suffit pas que la loi de Mariotte soit applicable, il faut encore que le coefficient de Gay-Lussac $\alpha=0{,}00366$, s'applique identiquement aux particules dissoutes et aux gaz. Or cette condition est douteuse d'après Ponsot, et d'après Lord Berkeley et M. Harteley. Aux fortes pressions surtout, la dilatation de la particule dissoute est à peine sensible même entre 4 et 24, tandis que, pour la molécule d'une vapeur comprimée, le coefficient α est supérieur à 0,00366.

Enfin, les expériences de M. Fouard (Journ. de Phys. 1911), montrent qu'avec des membranes en fulmicoton, les tensions osmotiques moléculaires changent, tout en restant à peu près égales entre elles, avec cette membrane particulière.

L'osmose semble donc être une fonction des membranes.

2o. D'autre part, les comparaisons isotoniques n'ont jamais été faites sur des mesures osmotiques, mais sur des déterminations cryoscopiques ou tonométriques.

L'identification de ces mesures reposant sur un cycle thermodynamique, a été considérée comme irréfutable. Pourtant, la légitimité de ce cycle est douteuse aux yeux de nombreux savants compétents. De fait, les résultats osmométriques ne sont aucunement comparables aux déterminations de Raoult. En effet, l'équation $\pi.V=RT$, fondement de l'osmométrie, indique que les comparaisons sont d'autant plus rigoureuses que les solutions sont plus diluées (moins concentrées, comme pour les gaz). Cette loi limite ne convient au contraire ni à la tonométrie, ni à la cryoscopie, où les solutions favorables dépassent parfois la concentration de 10%, et où les solutions diluées d'éloignent de plus en plus de la valeur théorique indiquée par la formule théorique:

$$K.M=0,02\frac{T^2}{L}$$

Cette formule donne aux Chimistes une impression de rigueur devant laquelle ils s'inclinent, et la valeur du poids moléculaire M qu'elle relie exclusivement à la température de fusion ou d'ébullition T du solvant et la chaleur latente correspondante L, apparait à leurs yeux, comme une détermination absolue et indépendante de toute hypothèse. Ils oublient que K est un coefficient spécifique cèlatif au corps dissout et que 0,02 est le quotient, par l'équivalent mécanique 425, du nombre R supposé égal à 847, pour la particule dissoute comme pour la particule gazruse.

En réalité, la formule $K.M=0,02\frac{T^2}{L}$ ne se relie à la thermodynamique que par un emprunt à l'équation de Clapeyron et elle n'est plausible que sous certaines conditions expérimentales que nous allons analyser.

Soient f et f′ les tensions de vapeur du solvant et de la dissolution, *n* le nombre de molécules contenues dans le poids P de la substance dissoute dont la poids moléculaire est M, d'où $n = \frac{P}{M}$; Raoult a exprimé sa loi (*Scientia.– Tonométrie*, p. 43) par l'expression

$$\frac{f - f'}{nf} = A, \text{ ou } \frac{df}{f} = A \frac{P}{M} \quad (I)$$

La diminution moléculaire de tension A est constante quelle que soit la substance dissoute.

Si l'on admet qu'en solutions étendues, l'équation de Clapeyron s'applique au solvant dont on néglige le volume liquide, on aura:

$$L = \frac{T}{42f} \ u \ \frac{df}{dT}$$

D'autre part, pour une molécule de vapeur normale:

$$uf = RT \quad \text{d'où: } L = \frac{T}{425} \times \frac{RT}{f} \times \frac{df}{dT} = \frac{R}{425} \times \frac{T^2}{f} \times \frac{df}{dT} \quad (II)$$

Comme: $\frac{R}{6y} = \frac{84f}{42f}$, c'est-à-dire sensiblement 2, si dans l'égalité II, nous remplaçons $\frac{df}{f}$ par sa valeur tirée de l'équation I, nous aurons:

$$L = 2 \frac{T^2}{dT} \times \frac{AP}{M} \quad \text{ou: } M \frac{dT}{P} = 2A \times \frac{T^2}{L}$$

Le coefficient $\frac{dT}{P}$ est l'abaissement de température provoqué par l'addition de 1 gramme de la substance à la masse de solvant employée. On peut l'assimiler à K et écrire: $KM = 2A \times \frac{T^2}{L}$. Cette formule montre que la valeur K×M est proportionelle à l'abaissement moléculaire de la tension de vapeur A. Or, A n'est voisin de 0,01 qu'à la condition qu'il réponde à des tensions voisines de 760 mm. d'après Raoult, (loc. citat. p. 46) qui insiste, en écrivant p. 56:

" $M \times \frac{dT}{P}$ dépend essentiellement de la pression atmosphérique, c'est-à-dire de la pression sous laquelle l'ébullition se produit."

Donc le remplacement de A par 0,01, est doublement approximatif, puisque la valeur 0,01 n'est pas rigoureuse et n'est, en outre valable qu'aux environs de la pression atmosphérique.

En résumé, les lois de la cryoscopie et de la tonométrie ne sont pas des lois limites comparables à celles de Mariotte et de Gay-Lussac mais des résultats limités par des conditions expérimentales assez étroites. De sorte que la thermodynamique h'a que des rapports éloignés avec ces phénomènes.

ETAT DES CORPS DISSOUS

Les lois de Raoult expriment, d'après leur auteur, qu'il existe un rapport entre le nombre *n* des particules dissoutes, et le nombre N des particules du solvant. Par exemple, la plupart des corps dissous dans la benzine au taux de 1 molécule dans 100 molécules de solvant, donnent pour abaissement cryoscopique moléculaire 49, voisin du nombre $52 = K \times M$, calculé d'après la formule:

$$K.M = 0{,}02 \frac{T^2}{L}$$

Au contraire, le phénol et les acides organiques donnent un nombre deux fois plus petit comme le montre le tableau suivant:

1 molécule phénol dans 100 molécules benzine donne $KM = 26$

1 molécule monochloracétique dans 100 molécules benzine donne $KM = 25{,}4$

1 molécule acide propionoque dans 100 molécules benzine donne $KM = 26$

1 molécule acide phénylacétique dans 100 molécules benzine donne $KM = 24$

Raoult, Van't Hoff et tous les autres auteurs, concluent que en solution benzinique, les corps précédents sont bimoléculaires, c'est-à-dire que leur particule dissoute (*dissolécule*), est formée par la juxtaposition de deux molécules simples. C'est là une conclusion nécessaire, si l'on admet que le rapport des particules dissoutes aux particules dissolvantes $\frac{n}{N}$ reste constant.

Les données cryoscopiques et tonométriques conduisant à la nécessité d'admettre que certaines particules dissoutes sont constituées par des molécules condensées, on peut se demander qui la valeur de KM calculée d'après la formule $KM = 0{,}02\ \frac{T^2}{L}$ oblige à supposer que la particule dissoute normalement est à l'état moléculaire. Il est facile de prouver le mal fondé de cette hypothèse.

Considérons l'acide acétique. D'après Cahours, la densité moléculaire de vapeur de ce corps se rapproche de la valeur $M^2 = (C^2H^4O^2)^2$ à mesure que la température s'abaisse: et elle s'en éloigne à mesure que l'on chauffe ou que l'on détend la vapeur. Donc, à température notablement inférieure à 120°, vers 18°, par exemple, la densité de ce corps correspondra à la formule condensée. La particule liquide, obtenue par compression de la vapeur, sera elle-même bimoléculaire, au moins. On retrouve ainsi la forme que Ramsay et Shields avaient fixée à $(C^2H^4O^2)^2 = 120$.

Puisque le rapport $\frac{n}{N}$ reste constant pour tout corps cryoscopé dans l'acide acétique, comme N correspond à 2 molécules, il faut que *n* corresponde aussi à 2 M, c'est-à-dire que chaque particule dissoute soit elle-même une particule double. Voici une singulière vérification de cette conclusion.

Si l'action dissolvante de l'acide acétique oblige les corps dissous dans son sein à prendre l'état bimoléculaire, elle agira de la même façon sur les gaz. Par conséquent le poids d'acide chlorhydrique sec, dissous dans 100 molécules d'acide acétique, qui correspondra à la valeur normale 39 de K.M sera, non pas $H\,Cl = 36{,}5$, mais $H^2Cl^2 = 71$. L'expérience sanctione cette prévision. Donc:

Les corps dissous dans l'acide acétique y prennent normalement la forme bimoléculaire.

Sous cette condition seulement, la formule $K.M = 0{,}02\ \frac{T^2}{L}$ permet de calculer le poids moléculaire M du corps dissous; mais le poids de la particule dissoute M′ s'obtiendra en remplaçant M par $\frac{M'}{2}$ dans la formule précédente et répondra au coefficient $K' = \frac{K}{2}$.

Tout porte à généraliser cette conclusion. En effet, d'après Raoult, l'eau dissoute dans l'acide acétique donne un abaissement normal, c'est-à-dire que son poids moléculaire 18 répond à la valeur 39 normale de K.M calculée pour l'acide acétique. Donc l'eau, comme les corps organiques, comme les chlorures métalliques anhydres, est bimoléculaire en solution acétique.

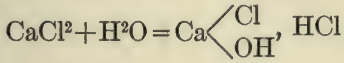
L'inverse semble absolument logique, non seulement par raison de réversibilité, mais pour ce motif qu'en dissolvant l'acide acétique liquide dans l'eau en excès, il n'y a pas d'effet thermique sensible. La cohésion seule de l'acide acétique liquide $(C^2H^4O^2)^2$ parait donc être modifiée par ce solvant; car s'il y avait dédoublement moléculaire, suivi d'une expansion des molécules simples $C^2H^4O^2$ dans le liquide, ce double effet nécessiterait une double absorption de chaleur.

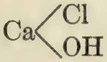
Alors l'acide acétique dissous dans l'eau, donnant comme le sucre la valeur normale $K.M=19$ propre à ce solvant, les dissolécules de ces deux corps y sont bimoléculaires. Au contraire, celles du gaz chlorhydrique donnant la valeur 38 correspond à une dissolécule HCl monomoléculaire, et non plus à $\frac{1}{2}$ HCl.

Dans cet ordre d'idées l'eau est un solvant comme un autre, et les remarquables expériences de M. Harry Jones, de Baltimore, trouvent une nouvelle explication. Par exemple, si l'abaissement moléculaire du point de congélation de $CaCl^2$ est 4 fois plus grand que celui qui résulte de la formule de Van't Hoff, c'est que:

1o. $CaCl^2$, comme NaCl, comme HCl, est monomoléculaire en solution, c'est-à-dire qu'il correspond normalement au produit $KM=38$;

2o. Au contact de l'eau, le chlorure s'hydrolyse manifestement car $CaCl^2$ ne peut plus s'extraire de la solution. Admettons

que  $CaCl^2+H^2O=Ca\left<\begin{matrix}Cl\\OH\end{matrix}\right., HCl$

les deux molécules  $Ca\left<\begin{matrix}Cl\\OH\end{matrix}\right.$ et HCl agissant comme 2 HCl sur le point de congélation, produiront un abaissement 4 fois plus grand que celui des corps organiques auxquels s'applique la formule de Van't Hoff.

CHAPITRE II

LES FORMULES RATIONNELLES

J'ai dit ailleurs et ici pourquoi ces formules de Van't Hoff sont plutôt des formules approximatives que des formules rationnelles, c'est-à-dire rattachées indubitablement aux deux principes fondamentaux de la thermodynamique.

Il n'en est pas de même de la loi de l'action de masse, qui est considérée aujourd'hui comme intangible. Pourtant la formule qui résume cette loi n'est pas à l'abri de la critique.

Depuis Guldberg et Waage, elle a pour forme:

$$\frac{p^m p'^{m'} \cdots}{q^n q'^{n'} \cdots} = \text{Constante}$$

en appelant: $p\ p' \ldots . q\ q'\ q'' \ldots .$les pressions partielles des corps $\chi\ \chi', \chi'', \ldots . \gamma, \gamma', y'', \ldots .$qui sont en équilibre sous la condition: $m\chi + m'\chi' + m''\chi'' = n\gamma + n'\gamma' + \ldots .$

M. Le Chatelier, analysant les résultats énoncés par Van't Hoff concernant la loi de l'action de masse et celle du déplacement de l'équilibre, est arrivé aux mêmes conclusions que le savant hollandais "par des considérations purement expérimentales," dit-il dans son Mémoire sur les *Equil. Chimiques.* (*Annales des Mines,* 1888 p. 109, 219 et 225.)

On sait que c'est sur l'artifice des parois semiperméables, découvertes par Traube et utilisées par Pfeffer, que Van't Hoff a basé sa démonstration rationnelle.

Appliqué à l'équilibre suivant:

$$4HCl + O^2 = 2H^2O + 2Cl^2,$$

le raisonnement de Van't Hoff est irréprochable dans les limites de température où les vapeurs H^2O et HCl existent sans décomposition; Il ne l'est plus pour les phénomènes de dissociation.

Précisément, c'est "en généralisant les conséquences déduites d'expériences de dissociation trop peu nombreuses" faites par Deville, Isambert et M. Lemoine, que M. Le Chatelier cite la formule générale:

$$\frac{p^m\ p'^{m'}}{q^n\ q'^{n'}} = \textit{Constante}$$

qu'il applique aussitôt à la dissociation du gaz carbonique:

$$2CO + O^2 = 2CO^2$$

et à celle du bromhydrate d'amylène (loc. cit. p. 109, 110), quoique, encore une fois, ni l'expérience ni la théorie n'autorisent cette généralisation.

Montrous d'abord expérimentalement que la formule précédente ne s'applique pas à la décomposition du bromhydrate d'amylène à température constante.

En prolongeant l'action de la température pour obtenir les densités du corps à l'état dissocié, M. Lemoine a observé pour l'équilibre:

$$\underline{C^5H^{11}B_2 = C^5H^{10} \times HB_2}$$
$$q \qquad\qquad p \quad p'$$

les fractions de décomposition suivantes:	à 175,°	à 185°,	à 200°,
sous la pression atmosphérique H	0,05	0,28	0.50,
sous la pression réduite a 1/10H	0,28	0,54	0,69

Si l'on calcule $\frac{pp'}{q}$, ici $\frac{p^2}{q}$ = *Constante* =, on trouve que *pour la fraction 0,05 la constante est proportionnelle à 6,57; et pour la fraction 0,28. la constante proportionnelle à 27,2.*

Donc, à 175,° ces deux valeurs de la constante sont très différentes. A 185,° elles sont proportionnelles à 27 et à 158, c. a. d. fort éloignées.

De même, dans la série des essais à 185°:

pour la fraction 0,50, la valeur de la constante est	1250,
pour la fraction 0,69, elle devient	384.[1]

Ces différences inadmissibles entre des nombres qui devraient être égaux, résultent de ce que la démonstration de Van't Hoff ne s'applique pas aux phénomènes de dissociation,

Je vais le prouver.

Dans la décomposition du gaz chlorhydrique par l'oxygéne, la théorie est admissible parce que les vapeurs H^2O et HCl ne sont pas décomposées à la température de l'équilibre. Mais supposons de l'eau dissociée dans le réservoir ABCD = V sous la pression totale P à T°. Appelons q,p et p' les pressions partielles de la vapeur, de l'hydrogéne et de l'oxygéne dans le mélange. Les pointillés CE et DE figurant des parois semiperméables: la première à l'hydrogéne, la seconde à l'oxygéne.

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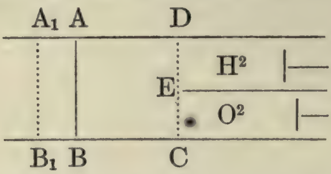
[1] Lemoine Compt Rend 20 avril 1891.— Reprenant ces expériences dans la vapeur d'al aniline c.a.d. à 182°, j'ai verifié qu'il fallait 2 heures environ pour obtenir l'équilibre de dissociation et constaté qui à cette température sous la pression 750 mm. la fraction djouié était 26,5%. C'est une bonne verification des idées et des expériences de M. Lemoine.

Je comprime des gaz séparément dans les cylindres H^2 et O^2



sous une pression très peu supérieure à p et à p' en même temps que je retire H^2O sous la pression q par le fond AB perméable à la vapeur. Je ne change rien, à aucun moment, dans le réservoir ABCD. Si la vapeur H^2O passée dans l'espace ABA_1B_1 conservait sa pression partielle q, l'opération inverse de ferait d'une façon réversible et le raisonnement de Van't Hoff continuerait à s'appliquer; mais l'espace ABA_1B_1 étant lui aussi à la température T°, la vapeur d'eau qui pénètre dans cet espace, sous la pression q se dissocie et ne conserve pas cette pression. La réversibilité du cycle isotherme de Van't Hoff est par conséquent détruite dès cet instant.

Pour parer à cette faute que j'ai souvent signalée, et en particulier dans ma "*Contribution a l'histoire de la Chimie*,"[1] on peut supposer que AB est un piston plein et non plus une paroi semiperméable. En déplaçant ce piston sous la pression totale P, on reconstitue et l'on défait à volonté la molécule d'eau dissociée par une suite d'opérations qui sont toutes réversibles.

Toutefois quand on passe d'un état [P, V, T] figuré par $ABCD = V$, à l'état $[P_1, V_1, T]$ figuré par $A_1B_1\ CD = V_1$, par exemple, le travail nécessaire pour revenir de $A_1\ B_1$ à AB a encore pour expression

$$\int VdP$$

Seulement, comme on ignore ici la relation qui unit P à V, ce travail ne peut s'exprimer en fonction de P, V, P_1 et V_2. Il dépend des conditions de l'expérience. Pour toutes les phases du cycle ci-dessus proposé, il a pour valeur:

$$P_1V_1 - P.V + \int V.dP - \lg \frac{p_1^{\,m}}{p^m} - \lg \frac{p'^{\,m'}_1}{p_1^{\,m'}}$$

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[1] Hermann Edit. 1910.

Puisque la valeur de $\int$ ne peut s'exprimer en fonction de P, V ou V_1 et P_1 il ne parait pas que $P_1 V_1 - PV + \int VdP$ soit égal à $\lg \frac{q_1 n}{qn}$ avec $q = P - p_1 - p$

Si l'on objectait que la démonstration de Van't Hoff n'est pas la seule, et que l'on peut arriver à la formule de Guldberg et Waage par l'hypothèse que l'entropie d'un système égale la somme des entropies de ses parties, il resterait deux points à élucider:

1o. Dire pourquoi les cycles fondés sur les parois semi-perméables conduisent à la loi des masses dans certains cas et non pas dans d'autres,

2o. Prouver que l'hypothèse basée sur l'entropie est un axiome irréfutable; ce que beaucoup de mathématiciens mettent en doute, et ce qui n'est peut être pas conforme à l'expérience, car voici des faits:

Cahours en traitant les éthers salicyliques par la chaux vers 250°, a obtenu des oxydes mixtes

I $CaO + C^6H^5O.CO^2C^2H^5 = CaCO^3 + C^6H^5 - O - C^2H^5$

Au point de vue mécanique et chimique, cette réaction semble déterminée par l'affinité de la chaux pour le gaz carbonique. Cette affinité répond à un dégagement de chaleur de 44000 calories

II $CaO + CO^2 = CaCO^3 + 44.000$ *cal.*

Cependant, bien que la chaux se combine à CO^2 dans ces conditions, j'ai constaté qu'avec de la chaux en grains, cette base n'intervient pas. On obtient à 225°.

III $C^6H^5O.CO^2.C^2H^5 = C^6H^5 - O - C^2H^5 + CO^2$

J'ai pu recueillir, en opérant avant le refroidissement complet des tubes, des proportions de gaz CO^2 libre qui, par rapport au gaz combiné, dépasse parfois le rapport: $\frac{95}{5}$ c. a. d. CO^2 *libre* 95%; CO^2 *combiné* 5% (dosage)

Donc l'énergie totale dépensée dans la réaction I qu'on la considere sous forme de chaleur totale de combinaison (Berthelot), ou de chaleur non compensée (Helmoltz—Clausius,) ou d'entropie (Gibbs), n'est pas la cause de la réaction I.

En d'autres termes, cette énergie totale n'est pas la résultante de la somme des énergies correspondantes aux réactions II et III et quoique la chaux se combine à CO^2 dans les circonstances de la réaction, cette énergie additionnelle n'est ni prépondérante ni déterminante.

CONCLUSION

Les théories basées sur l'assimilation de la molécule gazeuse & de la particule dissoute, & celles qui reposent sur la loi de l'action de masse, ne doivent pas être acceptées sans réserve.

A NEW METHOD OF MEASURING THE PRESSURE OF CORROSIVE GASES AT CONSTANT VOLUME

By George Shannon Forbes and Leslie Briggs Coombs
Harvard College, Cambridge, Mass.

Serious experimental difficulties are encountered in measuring the pressure of corrosive gases at constant volume and at high temperatures. The manometer devised for this purpose by Ladenburg and Lehmann[1] was a flattened quartz tube bent in the form of a Bourdon pressure gauge and provided with a pointer moving over a scale. This was used by Bodenstein and Katayama[2] in measuring the dissociation pressures of sulphuric acid and of nitric oxide. The behavior of this device is most exasperating, as one of the authors of this paper can testify from personal experience; it requires careful calibration; lastly, it is expensive and withal extremely fragile. Johnson's modification[3] of this manometer was a flattened glass tube coiled in a spiral, and terminated by a mirror. This spiral was enclosed in a mantle within which the pressure could be varied at pleasure. The mirror remained stationary so long as the external pressure on the spiral equalled the internal pressure. If a manometer is to contain a liquid, that liquid must have no appreciable vapor pressure of its own at the temperatures employed, and must not dissolve or react with the gases with which it is in contact. Neither mercury, sulphuric acid, glycerine, nor any other liquids hitherto employed can meet these requirements in dealing with vaporized acids, halogens and similar substances at high temperatures.

The present apparatus is easily constructed from materials available in every laboratory. The pressure gauge is outside the oven, and its manipulation is easily mastered. No calibration is required. It is adapted for demonstration or research on pressures of gases and vapors, as well as vapor pressures of liquids and solids, which otherwise could be studied only by quartz or glass manometers or by methods similar to those of Dumas or Victor Meyer.

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[1] Ber. d. deutsch. physik. Ges., *4*, 20 (1906).
[2] Z. Elektrochem., *15*, 244 (1909).
[3] Z. physik. Chem., *61*, 457 (1908).

The construction of the apparatus is evident from the diagram. The gas or vapor is contained in a bulb *A*, of any desired shape, and about 250 cc. in capacity. The bulb may be made of hard glass if necessary. Its stem *B* is sidenecked by a tube *C*, three millimeters in internal diameter and bent horizontally just above the point where it emerges from the electric oven *E*. This tube is wound rather closely with fine nichrome ribbon from *D* up to and beyond *G*. The small bulb *F* is filled before the determination with a finely powdered mixture of an equimolecular mixture of fused lead and silver chlorides. Various other pure or mixed salts could of course be used instead. This mixture was found to melt at about 350 degrees, that is, 140 degrees below the melting point of either of the pure chlorides. The tube is constricted at *H*, and the volume of this part of the system is further diminished by a section of glass rod *I*. An additional section may be introduced between *H* and *G*. The small connection *J* of vacuum tubing contains a smooth glass pearl which acts as a gas-tight seal unless the tubing is pinched at that point. A section of thermometer tubing *K* prevents any rapid flow of air in either direction. A fine capillary *L* which can easily be broken and sealed up again makes it possible to admit air or expel it from this part of the apparatus. Adjoining is a manometer provided with a flexible tube *N;* by raising or lowering the open tube *P* any pressure may be produced at *O*. This pressure is found by combining the barometric pressure with the difference in level between the mercury surfaces *O* and *Q*, which is read from the millimeter scale *S*. The readings of both barometer and manometer can be reduced to zero Centigrade by reference to tables.

If the pressure of the vapor of a liquid, as phosphoryl chloride, or of a solid, as iodine, is to be measured, a weighed amount is sealed up in a weighed capsule of glass tubing provided at one end with an exceedingly fine closed capillary. The stem *B* is held horizontally and the capsule allowed to slide in until the capillary is inserted in the small tube *T* fused into the bottom of the bulb. The bulb is evacuated to a few millimeters through the stem which is then fused off at some intermediate point. The chlorides in *F*, about one gram in weight, are carefully fused with a small flame, and the horizontal tube *FG* inclined by raising the bulb. The liquid runs toward *G* and easily forms a " drop " about one centimeter in length. Its small size and high temperature will preclude the solution of an appreciable amount of the gases in contact with it, judging by analogy from many researches carried out in the Harvard laboratory. A current barely sufficient to keep it in fusion is passed through the nichrome ribbon. The pressure of the residual air in *A* is now determined if necessary. The level in tube *P* is adjusted until on pinching the rubber tube *J* over the pearl, no movement of the drop is observed. Violent movements of the drop are rendered impossible by the great friction of the air in the thermometer tubing K. The drop easily responds to pressure changes of one or two-tenths of a millimeter in the manometer. Therefore the pressure in *A* can be equated exactly to the pressure at *O* unless the surface tension on opposite sides of the drop differs by reason of inequalities in temperature or the dissolving of gases. The first possibility is obviated by uniformity in the winding; the second seems unlikely in view of the small tendency of fused salts to dissolve gases, as already pointed out. Any other pressure in *A* can be determined in the same manner. The capsule containing the liquid is next broken by gentle shaking at a temperature where its vapor pressure does not exceed the pressure of the residual air (or nitrogen) in *A*. If a gas is to be investigated, it is admitted slowly into the evacuated bulb through a well-ground stopcock, and the drop is kept stationary by forcing in through *J* the proper amount of air. The same manipulation is carried out when the pressure of a gas or vapor is increased by raising the temperature of the oven. As the volume between the drop and the glass pearl is very small, the drop will not fall into *G* even if the valve in *J* is very carelessly manipulated while the pressure in *A* is increasing.

The pressure of the substance introduced is equal to the compensating pressure at *O* with two corrections. First, the pressure of the residual air or nitrogen at t^1, multiplied by the ratio $\frac{T^2}{T^1}$ must be subtracted. The second correction is necessitated by the fact that all the gas is not at the same temperature. Let V equal the total volume of the system and v the volume of the section *DR* of the tube *C*, in which the temperature is kept constant at t^1 by the nichrome wire. Imagine now the volume v reduced at the observed pressure p from t^1 to t, the temperature of the bulb. The gas will now occupy the volume $V-v\frac{t^1-t^{11}}{t+273}$. Now change the volume of the gas, at constant and uniform temperature t, back to V again when it will attain the pressure P.

$$P=p\frac{V-v\frac{t^1-t}{t+273}}{V}=p-\left[p\cdot\frac{v}{V}\cdot\frac{t^1-t}{t^1+273}\right]$$

The term in the bracket is the correction which must be subtracted from the observed pressure p to obtain P, the pressure which would be exerted by the same body of gas in the same volume in case the temperature of the bulb prevailed also in the tube wound with nichrome. For the values of V, v and t^1 in the apparatus described below, the correction never exceeded one millimeter.

The practicability of this method was established by determinations of the pressure of air and of chlorine, heated at constant volume to various temperatures. The oven used was cylindrical and was wound uniformly with several layers of nichrome ribbon insulated by asbestos. The temperature was controlled by a variable external resistance, and ample time was allowed to get a real equilibrium of temperature. Circular disks of asbestos accurately fitting the walls of the oven were fastened to the top and bottom of the bulb to keep that part of the oven uniform in temperature. The top and bottom of the oven also were protected by several thicknesses of asbestos. The temperature was measured by a suitably annealed thermo-couple of iron and constantan insulated from each other up to the junction by a glass tube. The terminals were plunged into tubes of mercury supported in a beaker of water whose temperature was read to tenths of degrees. The electromotive force was measured by the compensation method on a potentiometer so adjusted that when the terminals were at 25°, and the junction protected by a glass jacket was kept at

445° by sulphur vapor boiling under 760 mm., exactly 420 ohms on the potentiometer had to be included between the terminals to bring the d'Arsonval galvanometer to rest. An effort was always made, while measuring pressures, to halt the temperature of the oven at points where interpolation was unnecessary. Thus degrees were read directly from the apparatus and added to the temperature of the terminals. The readings were independent of the depth of immersion of the couple. The range between 25° and 445° was explored by readings in steam (100°), aniline (184°), nitrobenzene (209°), and diphenylamine (302°). The calibration of each of the two couples used was checked at frequent intervals. A curve was constructed showing the corrections necessary in order to reduce potentiometer readings to true temperature differences. The temperature at different points on the surface of the bulb was investigated and appeared to be constant within a degree. Still it was felt that the corrected temperatures might differ from the average temperature of the bulb by two or three degrees, and this difficulty, rather than errors in measuring pressures, is believed to be responsible for such irregularities as exist in the results given below.

Three independent experiments were carried out with air and three with chlorine. The results, exhibited in the table, show the practicability of the method.

V, the volume of the bulb and side tube back to the drop, was 260 cc., the stem *B* being sealed off each time at the same distance from the bulb.

v, the volume of the gas in the section *DR* (15 cm. long), as determined by weighing mercury in a measured section of the tube, was 1.3 cc.

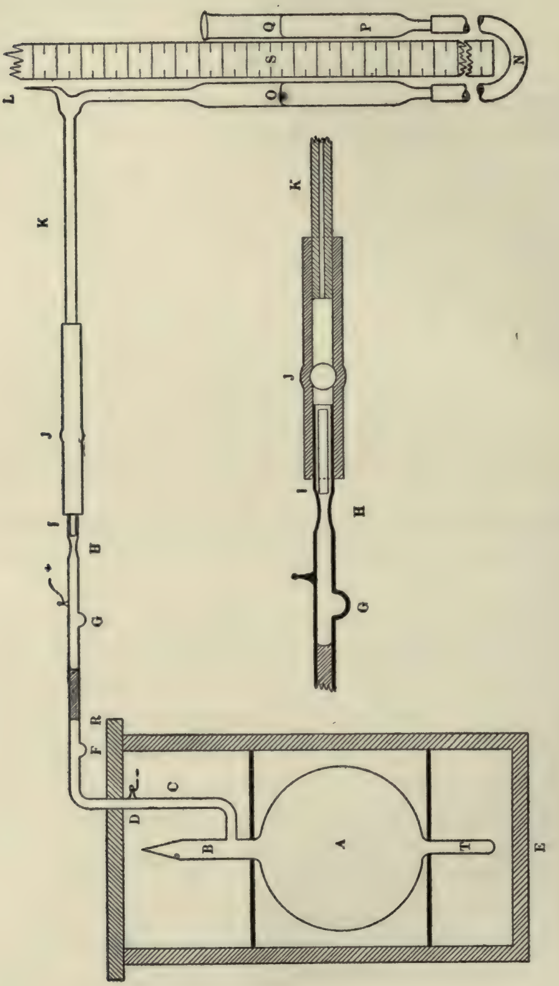
t^1, the average temperature of v, as determined by a thermocouple inserted in the tube in a special experiment, was 330 degrees.

T is the absolute temperature of the bulb found by adding 273 to the corrected readings of the thermo-couples..

p represents the pressure indicated by the manometer.

P is the same corrected for lack of uniformity in temperature as previously described.

The pressure P_x is calculated from P_n the pressure at t_n by the formula $P_x = P_n \cdot \frac{T_x}{T_n} \cdot (1 + 0.000028\,[t_n - t_x])$ where 0.000028 is the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value assumed for the mean coefficient of cubical expansion of soda lime glass at the temperatures noted.

All the measurements made are included in the table, except one, where time was lacking to reach a constant temperature, and one rejected for unknown but obviously gross error. It is interesting to note that the figures show the abnormally large increase in the temperature coefficient of chlorine at temperatures below 100°.

EXPERIMENT 1. (AIR)

tobs.	T corr.	pobs.	P corr.	P calc.
18	291	213.2	212.6	213.7
183	454	329.5	329.1	331.8
223.5	491.5	361.5	361.2	358.9
254	522.5	381.5	381.2	.....

EXPERIMENT 2. (AIR)

tobs.	T corr.	pobs.	P corr.	P calc.
21	294	207.5	207.0	206.2
265	532	370.4	370.2	370.7
287	554	385.0	384.8	385.4
308	575	399.5	399.4	399.6
328	595	413.5	413.5	413.4
348	616	427.5	427.5	427.9
362.5	631	438.0	438.1	.....

EXPERIMENT 3. (AIR)

tobs.	T corr.	pobs.	P corr.	P calc.
20	293	247.5	246.9	247.9
141.5	414.5	349.0	348.4	349.5
182	453	382.5	382.0	381.6
223	491	415.5	415.2	413.3
263.5	530.5	446.3	446.0	.....

EXPERIMENT 4. (CHLORINE)

tobs.	T corr.	pobs.	P corr.	P calc.
26.5	299.5	384.0	383.0	388.3
117.5	390	503.0	502.4	504.4
148	419.5	542.0	541.2	542.5
178.5	449	580.0	579.3	579.8
209	479	615.5	614.9	613.9
239	506	653.1	652.6	.....

EXPERIMENT 5. (CHLORINE)

tobs.	T corr.	pobs.	P corr.	P calc.
123	395.5	518.0	517.1	515.5
173.5	444	580.6	579.8	578.1
224.5	491.5	643.0	642.8	638.6
254.5	521.5	680.7	680.2	677.3
285	552	718.7	718.4	716.6
315.5	583	756.5	756.4	.....

EXPERIMENT 6. (CHLORINE)

tobs.	T corr.	pobs.	P corr.	P calc.
23	296	387.1	386.1	388.5
82	355	464.6	463.7	463.9
103	375	489.8	488.9	490.2
133.5	404	528.7	527.9	527.8
164.5	434	565.5	564.7	566.0
205	471.5	615.1	614.5	.....

In closing, it is a pleasant duty to acknowledge the courtesy of Simmons College, in whose laboratory a part of the work was carried out.

EQUILIBRIA IN SYSTEMS CONTAINING ALCOHOLS, SALTS AND WATER, INCLUDING A NEW METHOD OF ALCOHOL ANALYSIS

By Geo. B. Frankforter and Francis C. Frary
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The work of which this is abridged report,[1] was conducted with the primary purpose of studying the salting out of alcohol by potassium fluoride, and using the results as the basis of a method for the determination of alcohol. Aside from the work thus indicated, several other systems involving alcohols, salts and water were studied for comparison.

As one of the important phases of the problem there arose the question of the dehydration of the alcohol by potassium fluoride, as a matter of industrial importance.

The alcohols differ among themselves in their behavior toward salting-out reagents. It appears in general that the higher the molecular weight of the alcohol, the easier it is to salt it out. Potassium carbonate is the only salt known which has the power of salting-out methyl alcohol (Linebarger, Am. Chem. J., 1892, *14*, 381), while the carbonates, phosphates and hydroxides of sodium and potassium, the sulphates of sodium, ammonium cadmium, manganese, iron (ferrous), cobalt, nickel, magnesium and zinc, the nitrates and citrates of ammonium and potassium, sodium thiosulphate and silicate are all capable of producing two layers in ethyl alcohol under certain conditions. A very much larger number of salts precipitate propyl alcohol, and the higher alcohols are not miscible with water and hence are still more readily and completely salted out. The salting-out of ammonia by potassium carbonate or silicate (Procter, Chem. News, 1864, *9*, 25; Newth, J. Chem. Soc., 1900, *77*, 775) is the only example of the same phenomenon that I have found in the case of inorganic liquids, but among other organic liquids it is common.

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[1] For complete report see Research Bull. 1 of the University of Minnesota, which will be issued and may be obtained by applying to the President of the University.

(Firnhaber, Archiv des Apothekervereins Norddeutschland, 1824, *7*, 151; Linebarger, loc. cit., Brandes, Pogg. Ann., *20*, 586; Schiff, Lieb. Ann., *118*, 362; Procter, Chem. News, 1864, *9*, 25; Parmentier, Compt. rend., *104*, 686; Traube und Neuberg, Z. physik. Chem., 1887, *1*, 509; Bodländer, Z. physik. Chem., *7*, 308; Dodge and Gratton, J. Physik. Chem., 1898, *2*, 498; de Bruyn, Z. physik. Chem., 1900, *32*, 64; Ketner, Z. physik. Chem., 1902, *39*, 641; Fleckenstein, Physikal. Zeit., 1905, *6*, 419.)

The dehydration of alcohol by different salts has been studied by many chemists.

Of the various substances used, the commonest is lime, which gives a very strong alcohol, but causes quite a loss and is inconvenient on account of the large quantities of lime used.

The general theory of the drying action of a salt on a liquid, and the importance of choosing a salt which takes up a large proportion of its weight in water, has been discussed by Foote and Sholes (loc. cit.). Of the salts which can give a product containing over 97% alcohol, lime takes up over 32% of its weight of water, anhydrous copper sulphate 11%, anhydrous zinc sulphate 11%, magnesium sulphate 15%, barium chloride 7.7%, and potassium carbonate 13%. According to the results of Foote and Sholes, the lowest hydrates of these substances are in equilibrium with 99.5, 99.5, 99.4, 98.4, 99.3% alcohol respectively, at 25°. Potassium fluoride, absorbing 62% of its weight of water to form the lowest hydrate, and being in equilibrium at this point with 97.5% alcohol, certainly deserves to rank well among drying agents for liquids miscible with water. On account of its greater solubility, apparently, it absorbs the water and comes into equlibrium with the solution much more rapidly than most of the other drying agents.

For drying organic liquids, it is often convenient to use a sat

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(Soubeiran, Ann. 1839, *30*, 356; Mendeleef, Z. f. Chem., 1865, 260; Erlenmeyer, Ann., *160*, 249; Smith, Chem. News, *30*, 235; Lescoeur, Bull. soc. chim., 1897, (3), *17*, 18; Yvon, Compt. rend., 1897, *125*, 1181; Ostermeyer, Pharm. Zeit., *43*, 99; Z. anal. Chem., 1900, *39*, 654; Vitali, Boll. chim. farm., *37*, 257; Z. anal. Chem., 1900, *39*, 46; Bull. Chem. Zeit., 1900, *24*, 814, 845; Young, J. Chem. Soc., 1902, *81*, 707; Evans and Fetsch, J. Am. Chem. Soc., 1904, *26*, 1158; Winkler, Ber., 1905, *38*, 3612; Elektrochem. Werke Bitterfeld, Brit. Pat. 31, 567, Sept., 1906, and Ger. Pat. 175, 780, Sept. 1905; Klason and Norlin, Arkiv. Kem. Min. Geol., 1906, *2*, 1, J. Chem. Soc., 1906, *90*, i, 921; Kailan, Monatsh., 1907, *28*, 927; Plücker, Z. Nahr. Genussm., *17*, 454; Pozzi-Escot, Bull. assoc. chim. sucr. dist., *26*, 580; Hess. U. S. Pat. 996, 763; Chem. Fabr. Griesheim Elektron, Ger. Pat. 236, 591; Foote and Sholes, J. Am. Chem. Soc., 1911, *33*, 1309.)

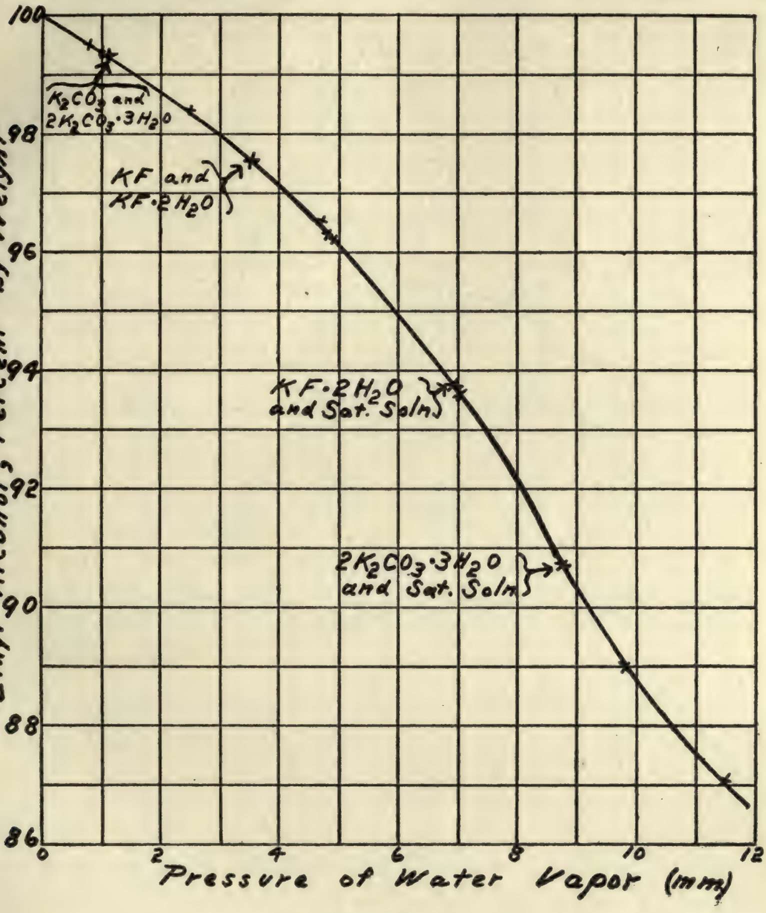

Figure 1
EQUILIBRIA BETWEEN ALCOHOL, WATER VAPOR, AND SALTS

urated solution of potassium carbonate. It gives less opportunity for loss of the liquid, mechanically, and the equilibrium is quickly reached. Any salt which is to be suitable for this purpose must have a good salting-out power, so that little of the liquid shall dissolve in it, and its saturated solution must have a low vapor tension. With the exception of the hydroxides of sodium and potassium, and potassium carbonate, the salts above mentioned

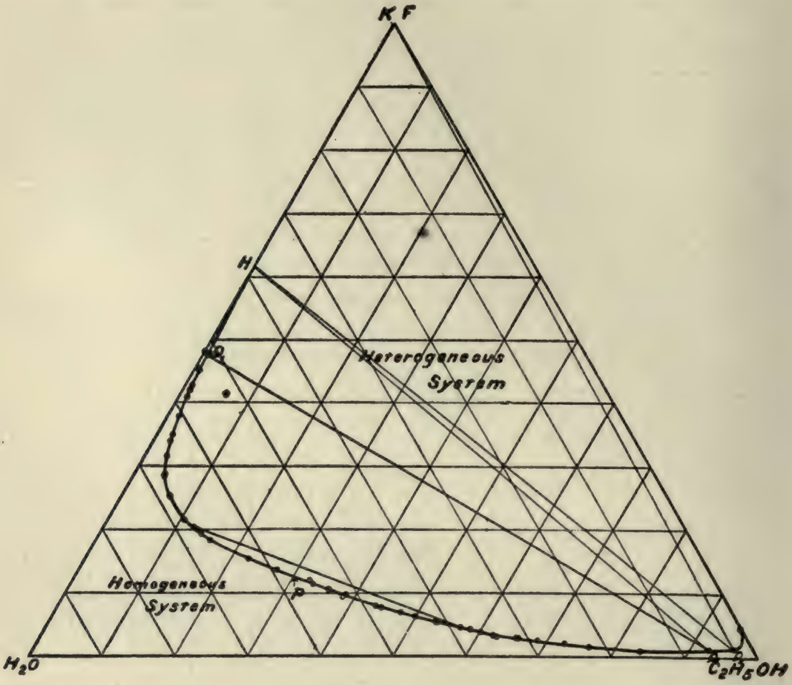

Figure 2
EQUILIBRIUM IN THE SYSTEM: POTASSIUM FLUORIDE, ETHYL ALCOHOL AND WATER

as having sufficient salting-out power to affect a solution of ethyl alcohol are not deliquescent, in their hydrated form, so the vapor pressure of the crystalline hydrate must be relatively high, and that of the saturated solution would be higher. By plotting the results of Foote and Sholes, the curve shown in Figure 1 is obtained, showing the vapor tension of the water in strong alcohol. The solutions of alcohol with which saturated solutions of potassium carbonate and fluoride and the solid hydrates are in equilibrium, when plotted on this curve give the approximate value of their vapor tension. It will be seen that while the vapor tension of the hydrate of potassium carbonate is lower than that of the hydrate of the fluoride, the saturated solution of the latter has a lower vapor tension than that of the former, and hence is a better

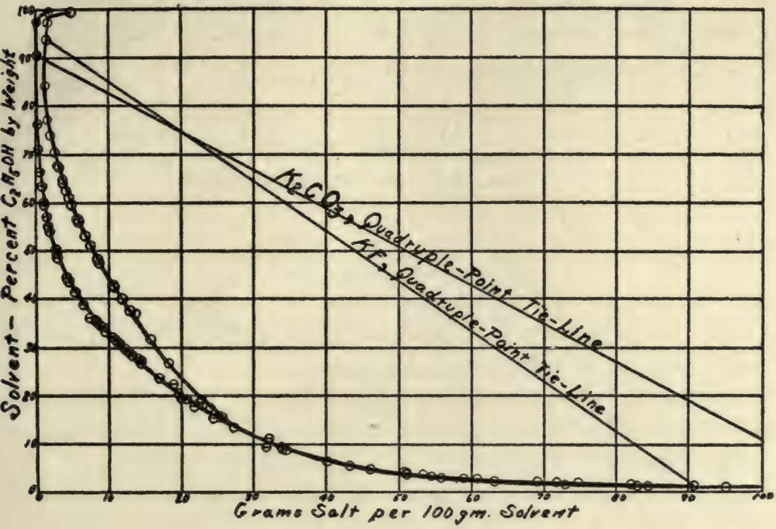

Figure 3

EQUILIBRIA IN SYSTEMS: POTASSIUM FLUORIDE, ETHYL ALCOHOL, WATER, AND POTASSIUM CARBONATE, ETHYL ALCOHOL, WATER, PLOTTED IN RECTANGULAR CO-ORDINATES

drying agent. From this curve it appears that, neglecting the effect of the small amount of dissolved potassium fluoride on the vapor tension of the alcohol, the vapor tension of the saturated aqueous solution of the fluoride is 6.9 mm. and that of the solid hydrate, 3.5 mm.

The salting-out properties of potassium fluoride seem never to have been mentioned in the literature, although they must have been noticed by Berzelius (Pogg. Ann., *1*, 11) who first described it, and by Rose (Pogg. Ann., 1842, *55*, 538) who precipitated some of the salt from solution as the hydrate by addition of alcohol.

The hydrate which this salt forms was first identified by Rose (loc. cit.) as $KF.2\ H_2O$; and Guntz (Ann. chim. phys., (6), *3*, 17) Fremy, (Ann. chim. phys., (3) *47*, 27) Mylius and Funk (Ber. 1897, *30*, 1716) and de Forcrand (Compt. rend. *152*, 1073) have verified the formula. The latter author has shown the existence of a hydrate $KF.4H_2O$ formed below 20°, and melting at 19.3°, while the other hydrate melts at 41°.

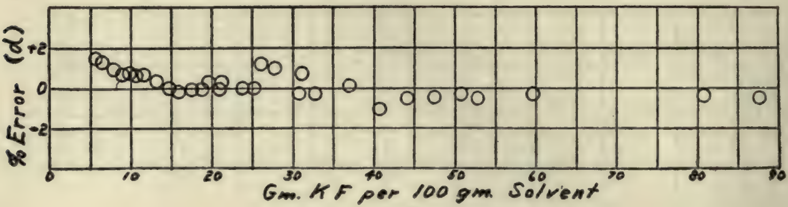

Figure 4
ERROR IN THE DETERMINATION OF ETHYL ALCOHOL IN THE PRESENCE OF METHYL ALCOHOL

Aside from the work above-mentioned, there is very little literature on neutral potassium fluoride.

The precipitation of a liquid from water by the addition of a salt comes under the general class of equilibria in ternary mixtures where the existence of two liquid phases is possible. The general theory of such systems, and the form of the isotherms obtained, have been discussed by Schreinemakers. (Z. Phys. Chem., 1897, *22*, 93, 515; *23*, 649.) There are four classes into which such equilibria are divided: (1) each of the three components forms a binary system having two liquid phases when mixed with either of the other components, (2) two liquid phases are found in two of the possible binary systems above-mentioned, but not in the third, (3) in only one of the binary systems can two liquid layers appear, (4) each component, mixed with either of the others, gives a system with only one liquid phase, *i. e.*, a solution of one in the other, and only when all three are present can two liquid phases exist. All the above classes refer of course to stable systems, and examples of each class have been studied. The salting-out of the alcohols here treated comes under the fourth class, since neither in the system alcohol-water, alcohol-salt (free from water) nor water-salt can two liquid layers be formed, but when all three are present in certain proportions, such layers are formed within certain limits of temperature. It is customary to represent the

(F. W. Clarke, Am. J. Sci., (3), *13*, 291; Kohlrausch, Wied. Ann., 1879, 1; Guntz, Compt. rend., *97*, 256; Tamman, Wied. Ann., *24*, 530; Petersen, Z. phys. Chem., *4*, 384; Ditte, Compt. rend., 1896, *123*, 1281; 1897, *124*, 29; Pauli, Z. Elektrochem. 1897, *3*, 474; Tanatar, Z. anorg. Chem., 1901, *28*, 255; Fox and Herz, Z. anorg. Chem., 1903, *35*, 129; Karadeef, Centr. Min., 1909, 728; C. A., 1911, *4*, 433.)

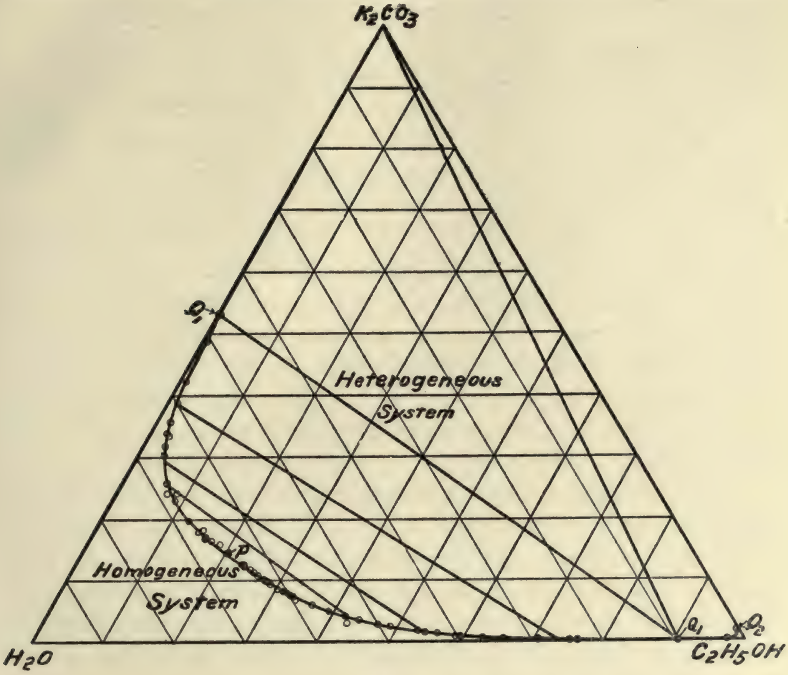

Figure 5
EQUILIBRIUM IN THE SYSTEM: POTASSIUM CARBONATE, ETHYL ALCOHOL, AND WATER

equilibrium in such ternary systems in triangular co-ordinates, and the theory of such representation is too well known to require repetition.

EXPERIMENTAL METHODS

The Binodal Curve. The point at which an inhomogeneous solution of the alcohol, salt, and water just become homogeneous, is a point on the binodal curve, and the determination of a number of such points enables one to plot this curve accurately. For the purposes of this investigation a synthetic method of determination was chosen, rather than an analytical one, as it appeared to be more rapid and also much more accurate. To make a series of such determinations, an Erlenmeyer flask fitted with a ground stopper was cleaned, dried, and weighed, and the dried salt weighed into it. In the case of potassium fluoride, the salt has been ignited and weighed in a covered platinum crucible and was simply transferred to the flask, and the crucible rinsed out to get the last traces. This method was adopted to avoid the absorption of water by the salt during the transfer and weighing. It was found that the amount of moisture absorbed while weighing the salt in the covered crucible was only about a tenth of a milligram per minute. After weighing the salt, water was added to dissolve it, the flask again weighed, and enough alcohol added to cause the formation of two layers. A trace of the solid dye used as indicator was now added, and the flask again weighed. Water was now added from a burette, with shaking, until the solution just became homogeneous, the flask weighed again, and the addition of alcohol and water repeated until a series of results was obtained.

All weighings were made on a Sartorius balance of ample capacity easily sensitive to 0.5 mg. with a load of 500 gm. on each pan, but weighings were only made to the nearest milligram. It is not claimed that the accuracy of the titration was generally greater than 0.1 or 0.2 gm., but the weighing was carried to milligrams to minimize cumulative errors in the quantities of alcohol and water present. When the flask had to stand long enough during a series to lose appreciably in weight, corrections were always made for such loss, which generally amounted to less than 30 mg. None of the flasks used showed any signs of etching by the fluoride, and weighing before and after use showed that the loss by such etching, and hence the contamination of the solution, were negligible.

Spirit Blue was used as an indicator, and gave very good results, except with potassium carbonate, which bleached it quickly. Phenol phthalein was later used with this salt, a few minute crystals of the solid being sufficient. The function of the indicator was to color the alcoholic layer, and render it easily visible when only a trace of it was present.

No attempt was made to work in a thermostat, or to control the temperature closer than two or three degrees, for two reasons. In the first place, preliminary experiments with potassium fluoride and ethyl alcohol showed the effect of such changes in temperature to be negligible, and in the second place such control would not be practical in the use of the figures obtained as the basis for an analytical method, and the possibility of obtaining accurate determinations under such conditions could most easily be determined by running a number of series under ordinary laboratory conditions, and comparing the points found. With propyl alcohol, where temperature was found to exercise more influence, more care was taken to control the temperature. The heat of the hands and the heat of dilution of the salts and alcohol tended to keep the temperature a little above that of the laboratory, and when not otherwise stated, the temperature of the solution may be assumed to have been between 23 and 26°C. Care was taken to avoid loss by evaporation or other causes during the course of the determination.

Specific Gravity Determinations. These were all made with 50 cc. pycnometers which had been carefully calibrated by correcting the thermometer against a certified thermometer graduated to 0°.02, and weighing full of water with all the usual precautions. The ground joints connecting the thermometer and capillary to the flask were tight, and by taking care to get the temperature of the room to within a degree of that of the substance to be weighed, it was easy to get very concordant results, duplicates generally agreeing to about 0.00005.

Hehner's table for ethyl alcohol and Dittmar and Fawsett's for methyl alcohol were used. For weak solutions of propyl alcohol the recent table of Doroshevskii and Rozdestvenskii (J. Russ. Phys. Chem. Soc., *41*, 1428; C. A., 1911, *5*, 409; Chem. Zentr., 1910, i, 812) was used, and for the stronger alcohol a table constructed as explained later under propyl alcohol. For the weak propyl alcohols, the determination was made at 15.0/15.55°, and considered to be close enough to the conditions of Doroshevskii and Rozdestvenskii (15./15.°).

MATERIALS

Methyl Alcohol. Kahlbaum's absolute methyl alcohol was used. Its sp. g. was taken at 15.55/4.00°, and three determinations gave 0.795762, 0.795875 and 0.795877. Dittmar and Fawsett give the specific gravity of absolute methyl alcohol at 15.55/4.00°

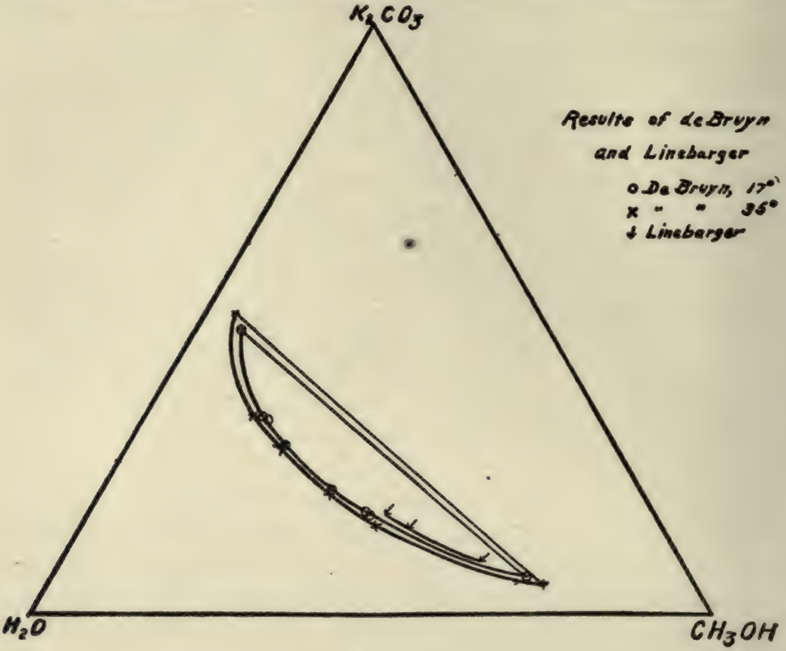

Figure 6
RESULTS OF LINEBARGER AND B. DE BRUYN

as 0.79589. The agreement was considered satisfactory, and the alcohol was figured as 100% pure.

Ethyl Alcohol.— Ordinary "95%" alcohol was digested with silver nitrate and caustic potash to remove aldehydes, and then twice distilled. Ten liters of this were prepared and carefully mixed, and stored in glass-stoppered bottles from which portions were removed to a smaller bottle for use as needed, thus preserving the main portion from contamination. From the average of four closely agreeing determinations of specific gravity, this alcohol was found to contain 91.28% by weight of absolute ethyl alcohol.

Propyl Alcohol.— For the determination of the binodal curves, Merck's normal propyl alcohol was used. It contained some water, and possibly some isopropyl alcohol. On distilling 100 cc. of it, 24 cc. came over between 91 and 94°C., and 63 cc. between 94 and 99°. Partial drying of this alcohol with anhydrous potassium

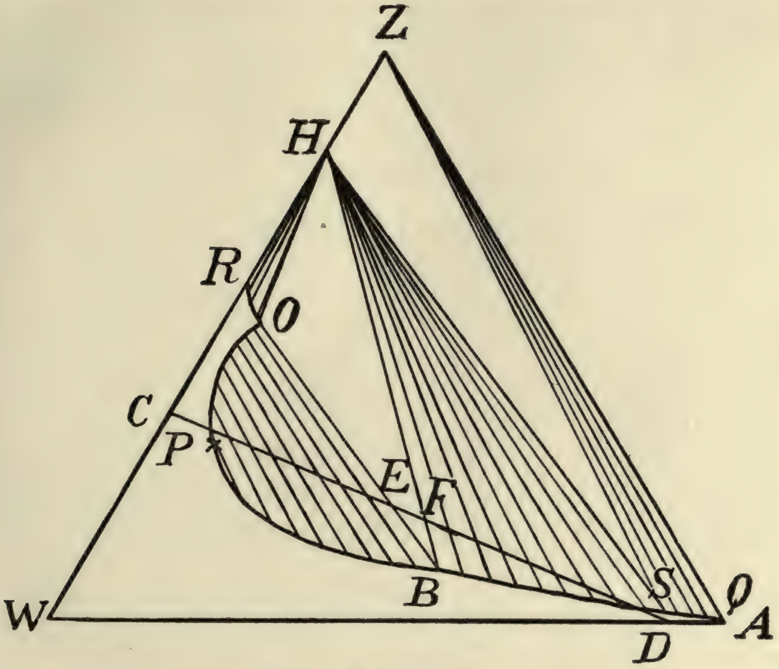

Figure 7
B. DE BRUYN'S DIAGRAM FOR THE SYSTEM: POTASSIUM CARBONATE, METHYL ALCOHOL, AND WATER

fluoride seemed to increase the proportion of the upper fraction. It is well known that the presence of water lowers the boiling point of propyl alcohol, the constant-boiling mixture boiling below 90°. The sp. g. of this alcohol at 20.0/15.55° was 0.80818. Some of the alcohol was treated with magnesium amalgam in excess, with which it reacted quite vigorously at first, and more slowly later. It stood with this for two weeks, with occasional shaking. Most of the action ceased within a few hours, but slow action was noticeable for several days. The clear liquid was filtered into a distilling flask and distilled, care being taken to protect the distillate from the air. Distillation began at 95°, and practically all of the liquid distilled over below 99°. At 15.55/15.55° two determinations of the sp. g. gave 0.80644 and 0.80647. The sp.

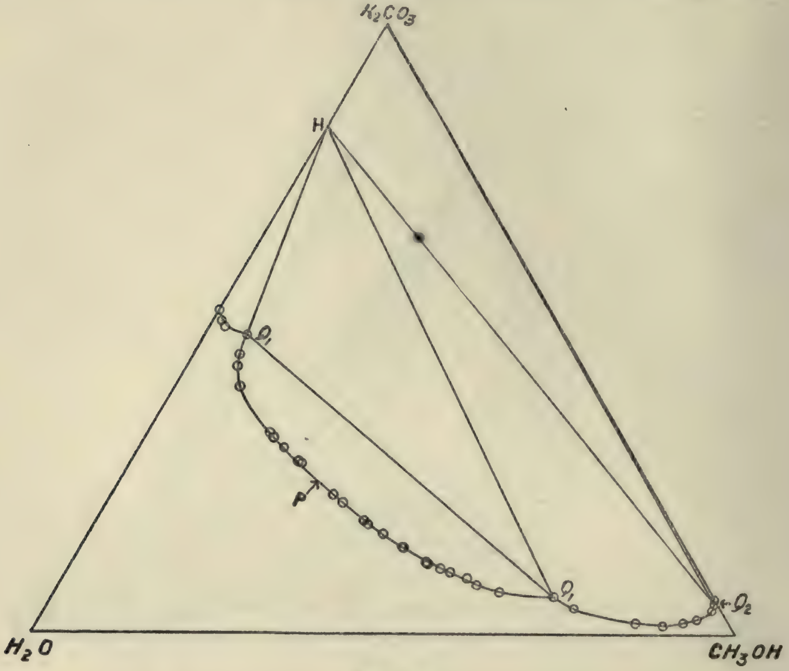

Figure 8
EQUILIBRIUM IN THE SYSTEM: POTASSIUM CARBONATE, METHYL ALCOHOL, AND WATER

g. of absolute propyl alcohol is given (Linneman, Ann. *161*, 26) as 0.8066 at 15, which is in good agreement with the above. Very recently Doroshevskii and Rozdestvenskii (loc. cit.) have found a higher value, but the details of the purification of their material are not available here. They appear to have been the first ones to work out a complete table of specific gravities of mixtures of propyl alcohol and water, but as their absolute alcohol was heavier than mine, I have used their table only for very dilute solutions. Using the absolute alcohol (71 gms.) described above, in a glass-stoppered Erlenmeyer flask, I added successive amounts of distilled water, making duplicate determinations of the sp. g. of the diluted alcohol resulting from each addition. The amount of diluted alcohol remaining in the flask after each set of determinations was carefully weighed before each addition of water and the weight of the absolute alcohol in it calculated from its known strength, to correct for losses of the diluted alcohol.

The following results were obtained:

Table I

Alcohol, per cent by weight	Specific Gravity at 20.00/15.55° (a)	(b)	Average
100.00	.80319	.80309	.80314
98.065	.80587	.80582	.80585
97.997	.80829	.80834	.80831
96.21	.81252	.81255	.81253
94.26	.81679	.81679	.81679
92.27	.82125	.82121	.82123
90.15	.82578	.82573	.82576
86.77	.83292	.83291	.83291

From the results obtained, the following table of specific gravities of mixtures of absolute propyl alcohol, from Merck's alcohol, was calculated:

Table II

% Alcohol	Sp. G. at 20./15.55°	% Alcohol	Sp. G. at 20./15.55°
100.00	.80314	92.00	.82185
99.00	.8058	91.00	.82395
98.00	.8083	90.00	.8261
97.00	.8108	89.00	.82825
96.00	.8130	88.00	.83035
95.00	.8153	87.00	.8325
94.00	.8175	86.00	.8346
93.00	.8197		

All strong propyl alcohol obtained in this work was determined from this table. According to it, the supply of Merck's propyl alcohol, used for most of this work, contained 98.07% by weight of the absolute alcohol.

Potassium Fluoride.— Merck's C. P. potassium fluoride was used. When freshly dissolved it was neutral to phenol phthalein, but quickly became alkaline. It contained only a trace of chloride, and appeared to be practically free from fluosilicates. No appreciable amount of sodium was shown on examination with the spectroscope, and a determination of iron and aluminum oxides

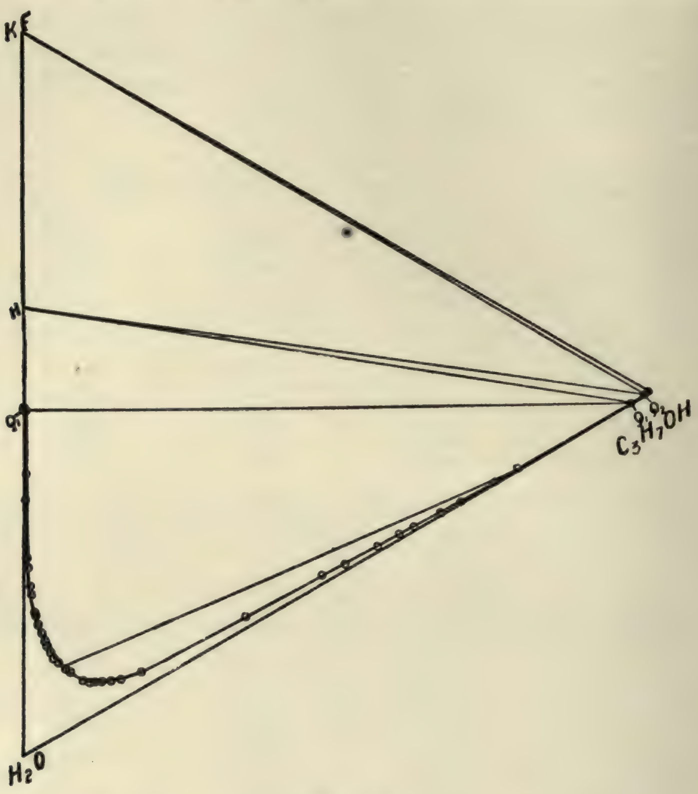

Figure 9

EQUILIBRIUM IN THE SYSTEM: POTASSIUM FLUORIDE, NORMAL PROPYL ALCOHOL, AND WATER

showed less than 0.003%. Tests for lime and magnesia gave negative results.

Potassium Carbonate.— Merck's potassium carbonate, "Highest Purity, Medicinal" was used. At first this was simply ignited and weighed, but the presence of small quantities of suspended matter, apparently oxides of iron and aluminum, was found to make it hard to get a good end point, so a quantity of the salt was dissolved in its own weight of water, filtered, and portions of this solution evaporated and ignited in platinum as needed. The solubility of the salt at room temperature was determined by evaporation and ignition of weighed quantities of the filtered saturated solution which had stood at least a week in contact with the hydrate. Duplicate determinations, two weeks apart, showed the solution to contain 53.05 and 53.07% by weight of the anhydrous salt.

Sodium Chloride.— Kahlbaum's salt, "C. P. zur Analyse" was used, the crystals being ignited for several minutes and cooled in a dessicator before weighing. Its solubility was determined as in the case of the carbonate, the saturated solution being found to contain 26.35 and 26.31% by weight of the salt. This value agrees well with those of Armstrong and Eyre (Proc. Roy. Soc., (A), *84*, 123, *79*, 566).

EQUILIBRIUM BETWEEN POTASSIUM FLUORIDE, ETHYL ALCOHOL AND WATER

This has never been studied elsewhere. Points on the binodal curve were determined at room temperature, according to the methods previously described. The effect of temperature change appears to be very slight. Careful determinations of the composition of the two layers at the quadruple point (paper, two liquid phases, solid hydrate) showed the upper layer to contain 92.69% alcohol, 6.07% water and 1.23% potassium fluoride by weight, while the lower layer contained only 0.67% alcohol by weight.

Two sets of conjugate solutions were analysed, to locate tie-lines and get an approximate idea of the position of the plait-point. They are shown in Figure 2, which presents graphically the equilibrium in the system. (For all the analytical data, see Research Bull. 1 of the University of Minnesota, which will soon be issued and may be obtained by applying to the President of the University.)

A good many experiments were performed in the attempt to locate accurately the position of the second quadruple point (vapor, liquid, anhydrous salt, hydrate), which will determine the extent to which the fluoride will dehydrate alcohol. Preliminary experiments showed that it was very easy to obtain alcohol containing about 96% by weight of absolute alcohol, but it appeared that the process of dehydration by repeated treatment with the anhydrous salt at boiling temperature, cooling, and decanting the solution did not raise the purity rapidly above

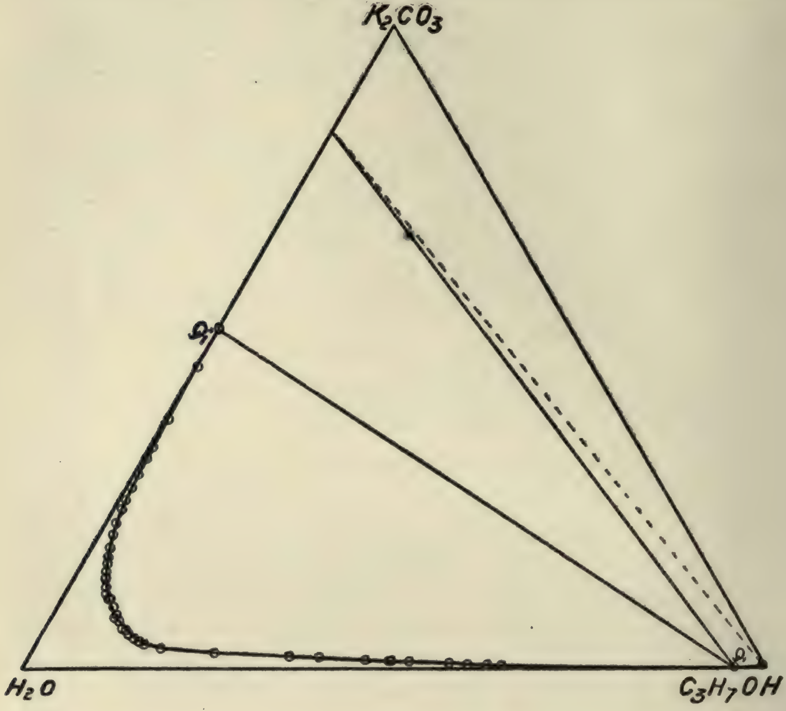

Figure 10
EQUILIBRIUM IN THE SYSTEM: POTASSIUM CARBONATE, NORMAL PROPYL ALOCHOL, AND WATER

this point. By long standing at room temperature, however, a sample of alcohol was obtained which gave a distillate containing 97.37% alcohol by weight. As the result of repeated treatment, (refluxing, cooling to –7°, decantation) with the anhydrous fluoride, an alcohol was obtained which after standing ten days at room temperature with excess of the hydrated salt, contained 1.52% by weight of anhydrous potassium fluoride, and gave a distillate containing 97.50% alcohol. Several experiments in grinding the anhydrous salt in a ball-mill with alcohol gave solutions containing this same amount of alcohol, or slightly less. This appears to be the solution at the quadruple point, and its composition was calculated to be: alcohol 96.05%, water 2.43%, potassium fluoride 1.52%.

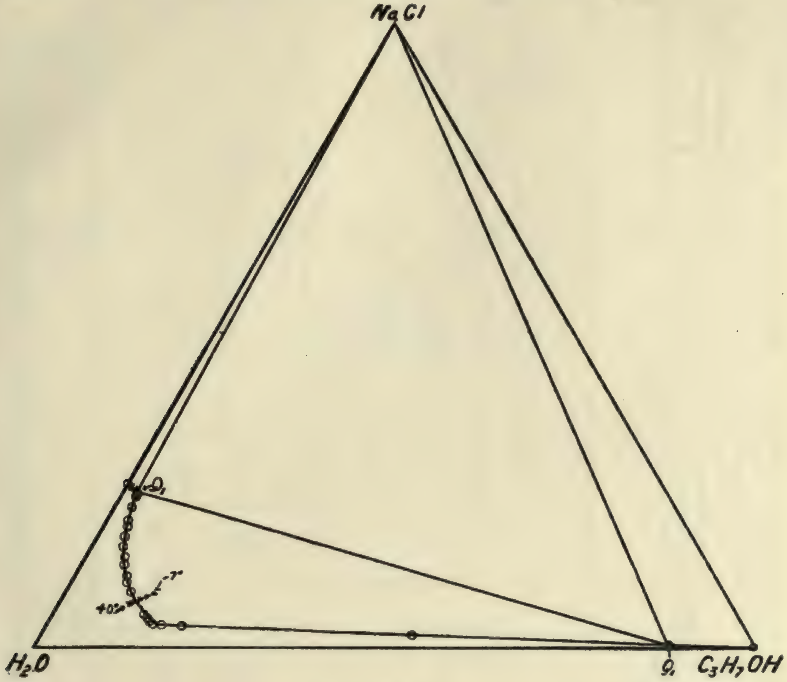

Figure 11
EQUILIBRIUM IN THE SYSTEM: SODIUM CHLORIDE, NORMAL PROPYL ALCOHOL, AND WATER

The solubility of the anhydrous salt in absolute (99.58%) alcohol was determined, the saturated solution being found to contain 4.57% by weight of the salt. It is to be noticed that although the saturated aqueous solution of the salt contains 48% of it by weight, (Mylius and Funk, Ber., 1897, *30*, 1716) yet the addition of water to the solution in absolute alcohol decreases the solubility of the salt in it to a marked extent: from 4.79 gm. per 100 gm. solvent in 99.6% alcohol to 1.54 gm. per 100 gm. solvent in 97.5% alcohol. A similar decrease in solubility with the first increase in water content of the alcohol appears also in the case of the fluoride with propyl alcohol, and the carbonate with all the other alcohols, but not with sodium chloride and propyl alcohol. It is interesting to note that the solu-

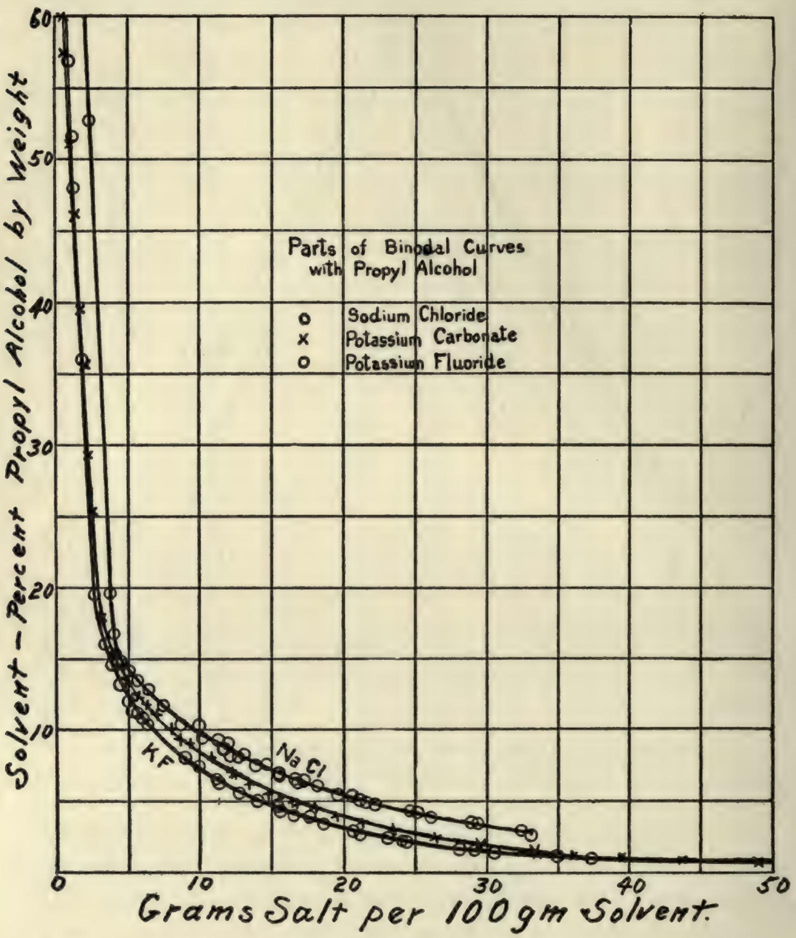

Figure 12

Equilibria in Systems: Potassium Fluoride, Normal Propyl Alcohol, Water, Potassium Carbonate, Normal Propyl Alcohol, Water, and Sodium Chloride, Normal Propyl Alcohol, Water

bility of the fluoride in absolute ethyl alcohol is about the same as in 60% alcohol.

In general, the solubility of a salt in aqueous alcohol decreases as the concentration of the alcohol increases. (Gerardin, Ann.

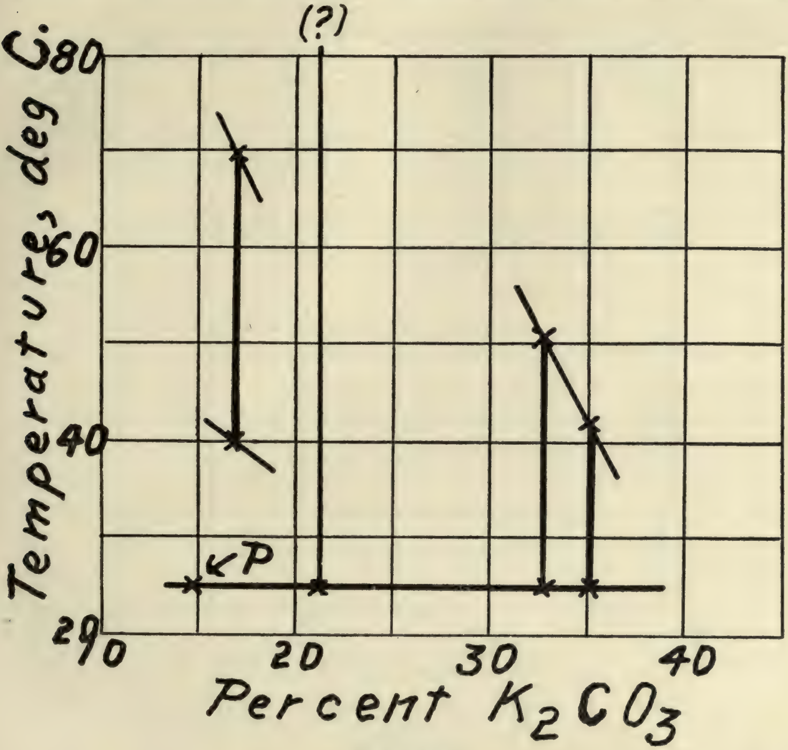

Figure 13
CRITICAL SOLUTION TEMPERATURES IN SYSTEM: POTASSIUM CARBONATE ETHYL ALCOHOL, WATER

Chim. Phys., (4), *5*, 129.) But L. de Bruyn has shown (Z. Phys. Chem. 1892, *10*, 782) that in absolute methyl alcohol the hydrated salts $MgSO_4.7H_2O$, $ZnSO_4.7H_2O$, $CoSO_4.7H_2O$, $NiSO_4.7H_2O$, $FeSO_4.7H_2O$, $NiSO_4.6H_2O$ and $CuSO_4.5H_2O$, were readily soluble, but were quickly precipitated again as the lower hydrates, (especially on adding a drop of water) or as lower hydrates in which part of the water of crystallization was replaced by alcohol. In 93% alcohol they were only slightly soluble, and less so in the more dilute alcohols down to 50%. He states that ethyl alcohol shows a similar behavior, but that it is less marked. Bödker (Z. Phys. Chem. 1897, *22*, 505) found that anhydrous cobalt and

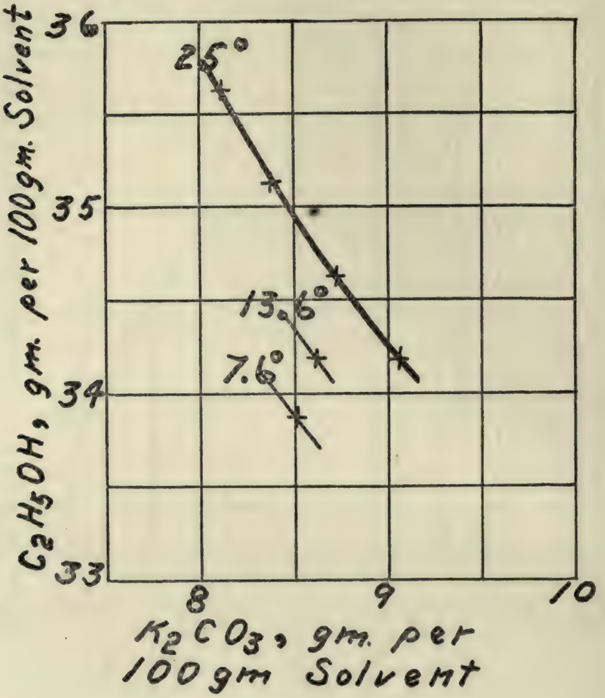

Figure 14

ISOTHERMS IN THE SYSTEM: POTASSIUM CARBONATE, ETHYL ALCOHOL AND WATER

copper chlorides were very soluble in absolute alcohol but that the addition of water caused the immediate precipitation of the hydrate. The results here shown with potassium carbonate and fluoride seem to be somewhat similar in principle, though of an entirely different class of salt, as far as the degree of hydration is concerned. But dilution of the solution of the anhydrous fluoride with water failed to produce precipitation of the hydrate, probably due to supersaturation phenomena, which were frequently noticed with alcoholic solutions of the hydrate which had been prepared at high temperatures and cooled out of contact with the solid phase. It is particularly noticeable that sodium chloride, which does not form a crystalline hydrate at ordinary temperatures,was least soluble in the strongest propyl alcohol.

Beside the well-known methods for the determination of alcohol by the specific gravity of a solution, and by its boiling point (Ebullioscope), many others have been studied in the attempt to find advantageous methods. Oxidation with either bichromate or permanganate has been studied by many.

The refractive index of mixtures of alcohol and water offers another method which has been well studied, and appears to be of practical value in some cases.

Indirect methods, depending on the change in specific gravity of a liquor after removing alcohol by evaporation and making up again to the same volume, have been discussed by a number of authors to determine the alcoholic content, (Duclaux, Ann. chim. phys., (5), *2*, 233; Gossart, Compt. rend., *113*, 537) as has also the lowering of the freezing point, (Gaunt, Z, Anal. Chem., 1905, *44*, 106, the solubility of cinchonine in chloroform containing alcohol, (Oudemans, Ann., *166*, 78, J. Chem. Soc., 1873; *26*, 533) the Pasteur drop reaction (Klocker, Centr. Bakt. Parasitenk., II Abt., *31*, 108, C. A., 1912, *6*, 136) and the color produced by cobalt salts in the presence of a sulphocyanide. (T. T. Monell, Chem. Zentr., 1877, 24.)

(Thresh, Chem. News, *38*, 251; Röse, Z. angew. Chem. *1*, 31; Bourcart, Bull. Soc. Ind. Mulhouse, *59*, 558, J. Chem. Soc., 1890, *58*, 1030; Frankland and Frew, J. Chem. Soc., 1891, *59*, 93; Grünhut, Chem. Zeit., *15*, 847, J. Chem. Soc., 1892, *62*, 1031; Benedikt and Neudörfer, Chem. Zeit., *16*, 77; Kuriloff, Ber. 1897, *30*, 741; Benedict and Norris, J. Am. Chem. Soc., 1898, 20, 293; Lassar-Cohn, Z. anal. Chem., 1899, *38*, 251; Argenson Bull. Soc. Chim., 1902, (3) *27*, 1000; Pozzi-Escot, Ann. chim. anal., 1902, *7*, 11; 1904. *9*, 126; Nicloux, Ann. chim. anal., 1904, *9*, 214; Marti , Rev. intern. Falsif., 1904, *17*, 48, J. Chem. Soc., 1904, *86*, ii, 520; Janak, Oesterr. Chem. Ztg., (2), *14*, 17, C. A., 1911, *5*, 2761.)

(Riegler, Z. anal. Chem., 1896, *35*, 27; Ling and Pope, J. Fed. Inst. Brewing, 1901, *7*, 170, J. Chem. Soc., 1901, *80*, ii, 628; Leach and Lythgoe, J. Am. Chem. Soc., 1905, *27*, 964; Ackermann and Steinmann, Zeit. ges. Brauw., *20*, 259, Chem. Zentr., 1905, ii, 1672; Ackermann, Ann. chim. anal., 1905, *10*, 171; Kamenetzky, Chem. Ztg., *31*, 257; Doroshevskii and Dvorzhanchiik, J. Russ. Phys. Chem. Soc., *40*, 101, *41*, 849, C. A., 1908, *2*, 2181, *4*, 135, 1403; Race, J. Soc. Chem. Ind., *27*, 547; Andrews, J. Am. Chem. Soc., 1908, *30*, 353; Frank-Kamenetsky, Z. angew. Chem., *23*, 293; Sidersky, Bull. assoc. sucr. dist., *27*, 1168, C. A., 1910, *4*, 2759, Ann. chim. anal., *16*, 142, C. A., 1911, *5*, 2143.)

(Blunt, Analyst, 1891, 221; Richmond, J. Fed. Inst. Brewing, 1896, *2*, 529, J. Chem. Soc., 1897, *72*, 193; Leonard and Smith, Analyst, *22*, 225; Pharm, Zentr., *49*, 971; Gunzel, Z. Nahr. Genussm., *18*, 206, C. A., 1909, *3*, 2717; Bonis, Ann. fals., *4*, 276, C. A., 1911, *5*, 3492.)

More closely allied to the method which I have to propose are the methods of Hagar (Chem. Zentr., 1888, 1512) and Böttger (Chem. Zentr., 1872, 742) who shake out the alcohol from essences with glycerine, and measure the increase of volume; Curtis, (J. Physic. Chem., 1898, *2*, 371) who titrates alcohol of 85% or over with toluene; and Bohlig (Z. anal. Chem., *25*, 19) who salts out the alcohol with potassium carbonate, and measures the volume of the layer obtained, standardizing the apparatus with known weights of absolute alcohol.

Methods involving the critical temperature of solution of alcohol-water mixtures with other liquids have also been worked out. The method of Crismer (Bull. assoc. belge. des Chemistes, *16*, 83, Chem. Zentr., 1902, ii, 3) using kerosene, is said to be very accurate, but is only applicable to very strong alcohol, while the method of Buboux and Dutoit, (Ann. Chim. Anal., *13*, 4, see also Duperthuis and Philippe, Mitt. Lebensm. Hyg., *1*, 188, C. A., 1911, *5*, 3118) using a mixture of aniline and alcohol, is only suitable for mixtures containing from 8 to 12% alcohol. An apparatus for the determination of alcohol, based on the solubility of ether in alcohol of various strengths (*i. e.*, the binodal curve in the system, alcohol, ether, water) has been patented and described. As specially pure ether and 98% alcohol are used to make the determination, it would hardly seem to be an easy and convenient method, and the accuracy may well be doubted.

If the binodal curve in the system containing a salt and aqueous alcohol has a small enough temperature coefficient, and can be determined with sufficient accuracy, it ought to be possible to add to a liquid of unknown alcoholic content enough of the salt to cause the solution to separate into two layers, and then, by the cautious addition of water, get the solution to be just homogeneous again. Now, if the weights used are known, the composition of the original alcohol can be found, since the composition of the solution which we have made homogeneous is represented by that point on the binodal curve which expresses the relation of the amount of salt to the whole solution or to the amount of solvent

(H. Kapeller, D. R. P., 213, 127, Oesterr. ung. Z. Zuckerind. Landw., *38*, 817, C. A., 1910, *4*, 232, 2348; Sidersky, Ann. chim. anal. appl., *15*, 105, Bull. assoc. sucr. dist., *27*, 562, C. A., 1910, *4*, 1793, 1648.)

present. Since there can only be one solution which contains this proportion of salt, on the line separating the homogeneous from the inhomogeneous solutions, this fixes the composition of the final solution definitely, and the weight of alcohol present can easily be computed.

While the method of Schreinemakers for representing such equilibria, as described on a previous page, is convenient and useful in many ways, it is not suitable for determination of the slope of the curve for analytical purposes, as triangular co-ordinates are inconvenient and the most important part of the curve comes at a point where the figure is very much compressed. For this reason, the results obtained have been calculated also on the basis of the weight of each component present in that quantity of the solution which contains 100 gm. of the solvent. Since the sum of the weights of water and alcohol here will be 100, this relation can be plotted in rectangular co-ordinates, the composition of the solvent being shown on one axis, and the amount of salt per 100 gm. solvent on the other. Such a curve also represents directly the solubility of the salt in alcohol of all strengths. In Figure 3 such curves have been plotted for both potassium fluoride and potassium carbonate, and show well the difference between these salts in their behavior toward alcohol. It is noticeable that at concentrations above 30 grams of salt per 100 grams of solvent the curves are nearly identical, although above 50 grams per 100 gm. solvent, the solubility of the alcohol in the solution of the carbonate is a little less than in that of the fluoride. It will be noted that the results for the fluoride form a smooth curve with which the individual results are in much better accord than is the case with the carbonate. The end point seemed to be more definite in the first case, and apparently the effect of temperature is less. For this reason the table recommended has been calculated on the basis of the fluoride curve, and is given in Table 3.

TABLE III

Determination of Alcohol by means of the Binodal Curve of the Ternary System: Water, Alcohol, Potassium Fluoride.

KF	Gm. per 100 gm. solvent C_2H_5OH	d	KF	Gm. per 100 gm. solvent C_2H_5OH	d
60	2.82	.10	30	11.36	.72
59	2.92	.10	29	12.14	.78
58	3.02	.10	28	12.99	.85
57	3.13	.11	27	13.92	.93
56	3.24	.11	26	14.94	1.02
55	3.36	.12	25	16.07	1.13
54	3.48	.12	24	17.33	1.26
53	3.61	.13	23	18.75	1.42
52	3.75	.14	22	20.26	1.50
51	3.90	.15	21	21.80	1.54
50	4.06	.16	20	23.40	1.60
49	4.23	.17	19	25.10	1.70
48	4.41	.18	18	26.90	1.80
47	4.60	.19	17	28.8	1.9
46	4.80	.20	16	30.8	2.0
45	5.01	.21	15	32.9	2.1
44	5.24	.23	14	35.0	2.1
43	5.48	.24	13	37.2	2.2
42	5.74	.26	12	39.4	2.2
41	6.02	.28	11	41.7	2.3
40	6.32	.30	10	44.0	2.3
39	6.65	.33	9	46.4	2.4
38	7.01	.36	8	49.0	2.6
37	7.40	.39	7	51.9	2.9
36	7.83	.43	6	55.1	3.2
35	8.30	.47	5	58.7	3.6
34	8.81	.51	4	62.8	4.1
33	9.37	.56	3	67.5	4.7
32	9.98	.61	2	78.6	11.1
31	10.64	.66			

To determine alcohol in an alcoholic liquid with this table, a stoppered flask is weighed, some freshly ignited potassium fluoride is weighed into it, a weighed amount of alcoholic liquid added, and the fluoride dissolved. From the probable alcoholic content of the liquid used, the proportions of liquid and salt are so chosen that there will be salt enough to cause the liquid to separate into two phases, *i.e.*, if a whiskey supposed to contain from 40-50% alcohol is being tested, the salt should be in the proportion of at least 12 gm. per 100 gm. whiskey, and then a separation will take place if the whiskey contained more than 39.4% alcohol, as indicated by Table 3. If the solution is now brought to approximately 25°, and water added cautiously, with frequent shaking, until the solution just becomes homogeneous, and the whole weighed again, the proportion of the salt present to the total weight solvent (whiskey plus water) gives by reference to the table, the per cent of alcohol in such total weight of solvent, hence the weight of alcohol in the sample. For rapid work, if 100 gm. of the liquid under examination be taken, and all weights carried only to the nearest tenth of a gram, reasonably accurate results could be secured in a very few minutes. If extreme accuracy is not desired, and care is taken in the preservation of the fluoride, it might be used without previous drying, making correction for water held as determined by one or two tests.

It is obvious that the method would not be very accurate in the presence of large quantities of dissolved solids, as in the case of a beer. But in the determination of alcohol in liquids where solids are absent, the good agreement of the data plotted in figure 3 with the smooth curve indicates that it would be satisfactorily accurate. One determination carried out on alcohol which had a sp. g. of 0.95223 (33.13% by weight) gave 33.18%. Heating the solution to 35° caused the solution to cloud a little, and when the titration was completed at that temperature, 33.53% of alcohol was found. The temperature coefficient for such a solution was evidently negligible within the range to which it would be easy to confine the temperature of the determination.

Since methyl alcohol is not precipitated by potassium fluoride, it was thought interesting to see what effect the presence of a certain amount of methyl alcohol would have on the determination of ethyl alcohol by this method. By weighing out some of the ethyl alcohol previously used, and mixing it with a weighed amount of absolute methyl alcohol, a solution was made containing 85.55%

ethyl alcohol, 6.72% methyl alcohol and 8.17% water by weight. The weight of methyl alcohol was thus 7.33% of the weight of absolute ethyl alcohol present. A series of determinations were made with this mixture and potassium fluoride, and the results are plotted in Figure 4. In plotting these, the quantity (d) chosen to be plotted against the concentration of the salt was the amount by which the per cent of ethyl alcohol in the solution was changed, *i.e.*, the error in the determination of the ethyl alcohol caused by the presence of 7.33% of its weight of methyl alcohol. A negative value indicates that too little alcohol would be found, on account of the increase in the solubility of the ethyl alcohol in the potassium fluoride solution, caused by the presence of the methyl alcohol, while a positive value indicates that too high a result would be found, the methyl alcohol here decreasing the solubility of the ethyl alcohol. It is surprising to note that in concentrated solutions there appears first a negative effect, over a wide range, and the methyl alcohol in the mixture acts as a solvent for the ethyl alcohol, then conditions appear to be reversed, although the results are not very concordant, then between 25 and 15 gm. salt per 100 gm. solvent, the determination is correct, within the limits of experimental error, and from this point down, the solubility of the ethyl alcohol is decreased by the methyl alcohol to a constantly increasing extent. This is a phenomenon worthy of further investigation, but it appears probable that within certain concentrations, ethyl alcohol can be satisfactorily determined in the presence of methyl alcohol by this method.

SYSTEM POTASSIUM CARBONATE ETHYL ALCOHOL WATER

Potassium carbonate is a salt which is much more often found in the laboratory than potassium fluoride, and therefore would be more convenient for analytical purposes. This system was therefore studied, and the position of the binodal curve determined. This salt was the first ever noted as having the power to salt out alcohol, as it is known that Raymond Lully (1235-1355) used and described it for that purpose. The composition of the solutions formed was first studied by Lescoeur (Bull. Soc. Chim., 1897, (3) *17*, 18), who determined the composition of the upper layer at the quadruple point: vapor, two liquids, solid.

A few determinations of points on the binodal curve were made by Linebarger (Am. Chem. J., 1892, *14*, 380) but the method used could not give accurate results, and the points determined all lie within a small part of the curve.

B. de Bruyn (Z. Phys. Chem., 1900, *32*, 63) determined the composition of the two solutions in equilibrium at the quadruple point. According to his own statements the accuracy of his alcohol determinations leaves much to be desired, duplicates differing by nearly two per cent being recorded. His determinations nearest room temperature are those at 17 and 35°. Bell (J. Phys. Chem., *9*, 531) has determined the composition of nine solutions lying on the binodal curve, and recently Cuno (Ber. Physik. Ges., *5*, 735; Ann. Physik, *25*, 346) determined the composition of eight sets of conjugate solutions. He states (Ann. Physik, *28*, 663) that his results agree fairly well with those of Bell, but plotting them together shows that his curve lies above that of Bell for its whole length, the difference in alcohol content between solutions of the same salt contents in the two curves being often nearly a per cent. His results are the most complete yet published, but his method of determination of the alcohol present (by the conductivity of the solution) might be open to question as the foundation of another analytical method. His determinations do not reach as far as the quadruple point.

As previously stated, some difficulty was experienced at times in obtaining good end points with this salt, so a larger number of determinations were made than in the case of the fluoride. The complete curve for the system is shown in Figure 5 for the first time. Although the formula of the hydrate of this salt has been in dispute, it was considered that the recent work of de Forcrand (Compt. rend., *148*, 1731) and Foote and Sholes (J. Am. Chem. Soc., 1911, *33*, 1309) identify the sesquihydrate as the one stable at ordinary temperatures and so this has been plotted in the figure. A number of conjugate solutions were analysed, to locate tie-lines, some of which have been plotted in the figure. The quadruple point where two liquid phases exist was determined; the upper solution was found to be alcohol, 90.56%, water 9.34%, potassium carbonate, 0.09%, and the lower one alcohol 0.28%, water 46.53%, carbonate 53.09%. The addition

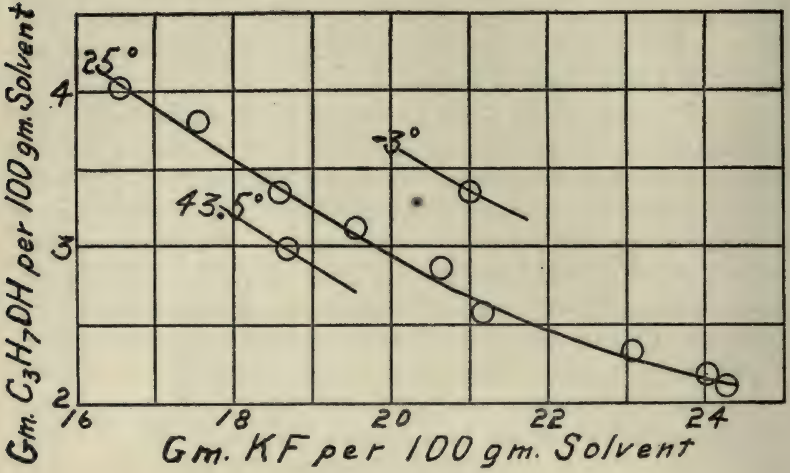

Figure 15
ISOTHERMS IN THE SYSTEM: POTASSIUM FLUORIDE, NORMAL PROPYL ALCOHOL, WATER

of the alcohol has thus not appreciably decreased the solubility of the salt in the water.

Saturated solutions of the salt in 97.5% and 99.6% alcohol were analyzed, and found to contain 0.054% and 1.64% of carbonate respectively. The same increase in the solubility of the salt in the anhydrous alcohol is to be noted here as in the case of the fluoride. As the mixture of anhydrous salt and hydrate is in equilibrium with 99.6% alcohol (Foote and Sholes, loc. cit.) this locates the other quadruple point.

In Table 4 will be found the approximate values corrected from the curve in Figure 3 over the range in which the curve is quite definitely determined. These values may be used for the determination of alcohol, in the same manner as those in Table 3, using dried carbonate, free from insoluble impurities, but the use of the fluoride appears more likely to give accurate results.

TABLE IV

Gm. per 100 gm. solvent		
K_2CO_3	C_2H_5OH	d
45	5.0	.2
44	5.2	.2
43	5.4	.2
42	5.7	.3
41	6.0	.3
40	6.3	.3
39	6.6	.3
38	7.0	.4
37	7.4	.4
36	7.8	.4
35	8.3	.5
34	8.8	.5
33	9.3	.5
32	9.9	.6
31	10.5	.6
30	11.2	.7
29	11.8	.6
28	12.5	.7
27	13.2	.8
26	14.0	.8
25	14.9	.9
24	15.8	.9
23	16.8	1.0
22	17.8	1.0
21	18.9	1.1
20	20.0	1.1
19	21.1	1.1
18	22.3	1.2
17	23.5	1.2
16	24.7	1.2
15	26.0	1.3
14	27.2	1.2
13	28.5	1.3
12	29.8	1.3
11	31.1	1.3
10	32.5	1.4
9	34.0	1.5
8	35.7	1.7
7	37.5	1.8
6	39.6	2.1
5	42.0	2.4
4	44.7	2.7
3	48.3	3.6
2.5	50.3	2.0
2	52.6	2.6

In Figure 3 the curves for both the fluoride and the carbonate are plotted in rectangular co-ordinates, and the quadruple-point tie-lines drawn. The determinations marked with a circle having a diameter drawn in are in the carbonate system, and it will be noticed that a number of them lie quite a distance from the line. The cause of this error was the uncertainty in the end point, due to suspended matter, which obscures the disappearance of the emulsion. If the carbonate is to be used for the analytical method, it must be freed from such matter by solution, filtration and evaporation. All weights above and elsewhere refer to the anhydrous salt. Where a large number of determinations were to be made, a strong solution might be prepared and standardized, and weighed portions used. A crystal or two of solid phenol phthalein is the best indicator.

The curve and table may be considered to be approximately correct for room temperature. Some experiments designed to show the influence of temperature will be discussed in the latter part of the paper.

SYSTEM POTASSIUM CARBONATE METHYL ALCOHOL, WATER

This system was first investigated by Linebarger (Am. Chem. J., 1892, *14*, 380), who made three determinations of points on the binodal curve. As shown in Figure 6, his results are evidently far from accurate, as they lie on a curve which must be true for temperatures near zero. De Bruyn (Z. Phys. Chem., 1900, *32*, 63) determined the position of the quadruple point at 17 and 35°, three other tie-lines on the binodal curve at the first temperature and two at the second. He recalculated Linebarger's results and showed their inaccuracy, and gave a general ("schematisch") curve to show the form of the isotherm. This is reproduced in Figure 7, to compare with the diagram of the isotherm which I have determined at room temperature (Figure 8) and the plot of the actual results obtained by him and by Linebarger (Figure 6). The only other work which appears to have been done on this system is that of Wrewsky (J. Russ. Phys. Chem. Soc., 1900, *32*, 593, J. Chem. Soc., 1901, *80*, ii, 56) who showed that the vapor pressure of the system increased with the proportion of the salt present. He showed that, as was to be expected, the two layers formed in the system had the same vapor pressure, the partial pressure of the water being lowered and that of the alcohol raised by the presence of the salt. He also studied the effect of temperature on the vapor pressure of the system.

As potassium carbonate appears to be the only salt which is capable of precipitating methyl alcohol at ordinary temperatures, this system was studied to see how closely it resembled the others. The binodal curve was determined, as in the other cases. Determinations of the composition of the two layers in equilibrium at the quadruple point were made by the same methods as in the other cases. The upper layer contained: methyl alcohol, 75.85%, water 17.83% and potassium carbonate 6.32%. The lower layer contained: methyl alcohol 6.10%, water 44.85% and potassium carbonate 49.05%. Several determinations of the solubility of the carbonate in stronger solutions of methyl alcohol were made. Samples of methyl alcohol containing 86.7, 90.5, 96.2 and 100% by weight of the alcohol gave solutions which contained respectively 2.05, 1.56, 2.72 and 5.64% by weight of potassium carbonate. Two other solutions, obtained in the process of locating the upper quadruple point (vapor, liquid, anhydrous salt, hydrate) were analysed and found to contain (a) alcohol 90.96%, water 7.06%, carbonate 1.98% and (b) alcohol 94.74%, water 0.87%, carbonate 4.39% by weight, respectively.

The determination of this upper quadruple point, by dehydration of 90% methyl alcohol with the ignited and pulverized carbonate, showed that at that point the solvent (or distillate if the solution be distilled) contains 99.35% alcohol by weight, while the solution as a whole contains alcohol 94.14%, water 0.33% and potassium carbonate 5.53% by weight.

Since the lower layer at the quadruple point (vapor, two-liquid layers, hydrate) contained only 49.05% carbonate, while the saturated aqueous solution contained 53.06%, attempts were made to get points along the line joining these two points. Two determinations were made by adding known quantities of the alcohol to strong aqueous carbonate solutions, and then water in small quantities until the salt precipitated had just redissolved. These and all the other determinations have been plotted and are shown in Figure 8.

SYSTEM POTASSIUM FLUORIDE, PROPYL ALCOHOL, WATER

The binodal curve was determined at room temperature as in the other systems, and the results are plotted in Figures 9 and 12. Experiments showed that the influence of temperature on the position of the binodal curve was quite marked in all cases in which propyl alcohol was one of the components of the system. Some observations on the effect of such changes at several points in the curve were therefore made, and are discussed under a later heading. (Temperature coefficients and critical solution Temperatures.) Determinations of the composition of the two liquid layers in equilibrium at the quadruple point were made as in the other systems, and the lower solution was found to contain 47.62% potassium fluoride and 0.039% propyl alcohol by weight, while the upper solution contained 96.78% propyl alcohol and 0.17% potassium fluoride. A determination of the solubility of potassium fluoride in 99.6% propyl alcohol showed that the saturated solution at room temperatures contained 0.34% of the anhydrous fluoride. One tie-line was investigated, the upper solution by analysis containing 78.91% of the alcohol and 0.31% fluoride by weight, while the lower solution contained 9.67% fluoride by weight. This tie-line has been drawn on Figure 9.

A determination of the composition of the liquid layer at the second quadruple point (vapor, liquid, anhydrous salt, hydrate) showed it to be: propyl alcohol, 98.44%, potassium fluoride, 0.28%, water, 1.28% by weight.

SYSTEM POTASSIUM CARBONATE, PROPYL ALCOHOL, WATER

The determinations of points on the binodal curve were made as in the other systems, and are plotted in Figures 10 and 12. The temperature of the solution was frequently tested during each series of determinations, and kept between 22 and 26°. Some determinations of the effect of change of temperature on the position of the binodal curve were made, and are discussed later. Duplicate determinations of the amount of carbonate in the lower solution at the quadruple point gave 53.05 and 52.89%, or practically the same as in saturated solutions of the carbonate at room temperatures (53.06%). A determination of the propyl alcohol content, in the distillate from about 300 gm. of the solution, showed this to be only 0.02% by weight. The upper solution contained 0.017% by weight of the carbonate, and 95.83% of propyl alcohol. It will be noted that as in the case of the quadruple point determinations with ethyl alcohol, the upper layer in the system containing potassium carbonate is a weaker alcohol than in the system containing the fluoride. This indicates as previously shown, that the saturated solution of the fluoride has a lower vapor tension than that of the carbonate. Determination of the solubility of the anhydrous carbonate in 99.6% propyl alcohol showed that the saturated solution under ordinary conditions contained 0.031% of the salt. The fluoride is therefore ten times as soluble as the carbonate in absolute propyl alcohol at their respective quadruple points. The other quadruple point, (vapor, liquid, anhydrous salt, hydrate) was not determined, as from the known vapor pressure of the hydrate of the salt, this point would undoubtedly lie within a few tenths of a per cent of 100% alcohol, and unless a quantity of specially pure alcohol was available, so that the actual gravity of the absolutely pure alcohol, carefully dried, could be obtained, it would be a waste of time to attempt the determination of this point.

SYSTEM SODIUM CHLORIDE, PROPYL ALCOHOL, WATER

As an example of a salt only moderately soluble in water, not capable of crystalllzing with water of crystallization under ordinary conditions, and possessing obviously a low affinity for water, sodium chloride was chosen as the precipitant to compare with potassium carbonate and fluoride. The binodal curve was determined as in the other systems, and the determinations are plotted in Figures 11 and 12. The first three series of determinations were made at room temperature, but without special care to control the temperature. In the last series, containing the solutions high in alcohol, where it would exert an influence that might be very disturbing, the temperature was taken frequently, and kept between 23 and 25°. The fact that those determinations in this series which fall within the limits of concentration covered by the other two series check well with them would indicate that the temperature in these series was not seriously different from that assumed (23 to 26°). As we do not have in the case of sodium chloride the relatively large heat of dilution which is found with the other two salts, the only factor tending to raise the temperature unduly was the heat of the hands, and the effect seems to have been negligible.

Determinations of the effect of temperature on the equilibrium showed that this is a much greater factor than in the case of the other two salts. This will be discussed in detail under the next head.

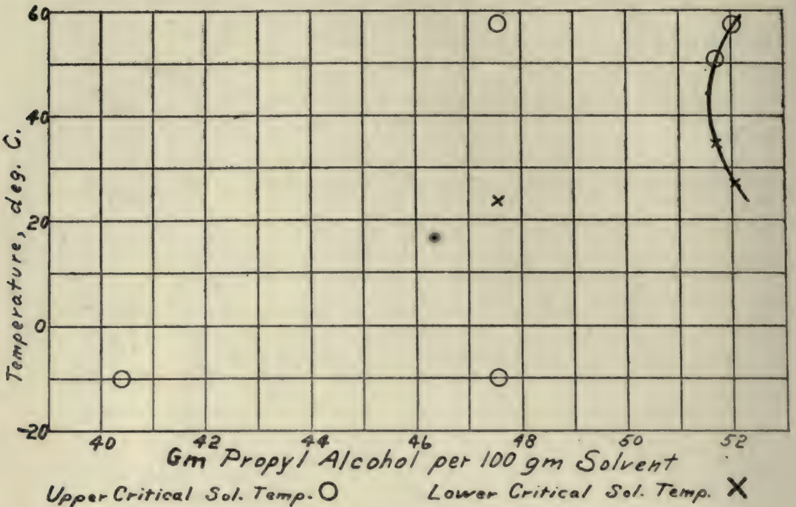

Figure 16

Upper and Lower Critical Solution Temperatures in the System: Potassium Carbonate, Normal Propyl Alcohol, Water

There is only one quadruple point in this system, as the salt does not form a crystalline hydrate at this temperature. The upper layer at this quadruple point contains 87.70% propyl alcohol and 0.55% salt by weight, while the lower layer contains 2.47% propyl alcohol and 24.90% salt. The saturated aqueous salt solution contained 26.33% of salt. The precipitation of salt from a saturated solution by addition of propyl alcohol has been studied by Armstrong and Eyre (Proc. Roy. Soc., (A) *84*, 123) and their determinations have been plotted in Figure 11 to give the line joining the saturated salt solution with the lower layer at the quadruple point.

Parts of the binodal curves for the three systems involving propyl alcohol have been drawn in rectangular co-ordinates in Figure 12. It will be noticed that the curves are in general parallel, but the curve for the carbonate lies above that for the fluoride at concentrations from three to forty grams of salt per 100 gm. solvent, and below it for concentrations outside these limits. This is exactly the reverse of the condition of things shown in

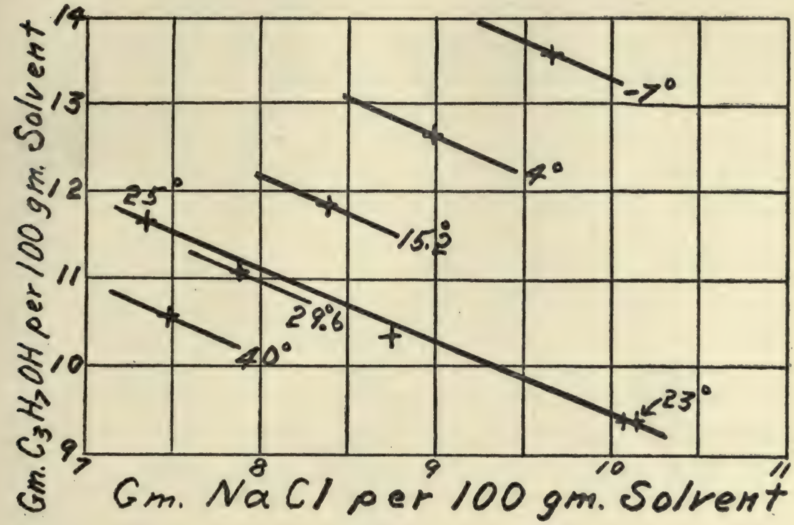

Figure 17
Isotherms in the System: Sodium Chloride, Normal Propyl Alcohol, Water

the systems involving ethyl alcohol (Figure 3) and would indicate that the relative salting-out power of different salts depends to a certain extent on the individual substance treated, and not, as some authors have stated, entirely upon the anion and cathion of the salt. The fact that sodium chloride, which is here shown to be nearly as good a salting-out agent as potassium carbonate for propyl alcohol, does not salt out ethyl alcohol at all, although it is relatively insoluble in strong alcohol, is another indication that we cannot reason from a few isolated cases to form a general theory of the salting-out process.

TEMPERATURE COEFFICIENTS AND CRITICAL SOLUTION TEMPERATURES

By the critical solution temperature of a mixture we understand that temperature at which the solution just becomes homogeneous. We may then distinguish between upper and lower critical solution temperatures, according as warming or cooling of the solution at that temperature produces homogeneity. For tenary systems a general theory of the critical solution temperatures has recently been given by Timmermans. (Z. Phys. Chem., *58*, 129.) He considers that all liquid pairs have in reality both an upper and a lower critical solution temperature, although neither or only one of them may be experimentally realizable. For the case of miscible liquids, such as those studied in this work, he assumes that the upper critical temperature lies below the lower critical temperature, and that the addition of a salt has the effect of either raising the upper critical temperature or lowering the lower critical temperature. If this effect is great enough, the upper critical temperature may come to its normal position above the lower critical temperature, and we have the possibility of the formation of two layers (salting-out) between these two temperatures.

The theoretical requirement that the salt be insoluble in one of the pair of liquids and quite soluble in the other in order to produce separation, does not seem to be rigidly necessary. It has been shown in this work that while potassium carbonate salts out methyl alcohol, it dissolves to the extent of over 6 gms. per 100 gms. solvent in the absolute alcohol, and in some of the other cases the solubillty of the salt in the alcohol is not small. But in all cases the solubility in alcohol containing some water is fairly small; it appears then that the theoretical statement should refer only to the solubility of the salt in mixtures containing a large excess of either component, and not to the pure liquids.

For the system: potassium carbonate, ethyl alcohol, water, Cuno (Ann. Physik, *25*, 346) has shown that the different isotherms representing the binodal curve all cross at or near the plait-point, and this point would then be independent of the temperature and a solution at this point would not cloud (become inhomogeneous) on either warming or cooling. Solutions containing more alcohol than this critical solution will cloud on cooling but remain clear on heating, (*i. e.*, are at their upper critical temperature) while those with less alcohol cloud on warming but remain clear on cooling (are at their lower critical temperature).

A similar phenomenon in the system: dextrose, water, acetone, has been described by Krug and McElroy (J. Analyt. Appl. Chem., 1892, *6*, 153, 188); and Traube and Neuberg (Z. Phys.

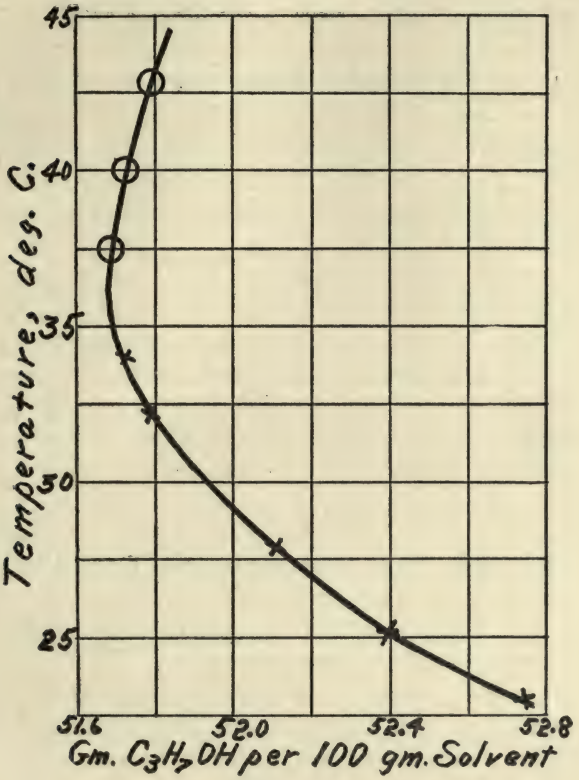

Figure 18

Upper and Lower Critical Solution Temperatures at Constant Salt Content, in the System: Sodium Chloride, Normal Propyl Alcohol, Water

Chem., 1887, *1*, 509) in the system: ammonium sulphate, ethyl alcohol, water, have found that the upper layer of two conjugate solutions is always at its upper critical solution temperature and the lower one at its lower critical temperature.

But Cuno also found that in the case of the lower ones of certain conjugate solutions, while they were at their lower critical temperature at 25°, an upper critical temperature could also be found above this. Thus with a solution containing 35.19% of carbonate by weight, the solution was inhomogeneous between 25 and 42°, while another solution containing 32.85% of the salt was inhomogeneous between 25 and 51°. A solution with 21.16% salt was clear below 25°, but cloudy from that point up to 80°, which was as high as it could be tested. Therefore, with increasing salt content in the upper layer, the temperature interval between the upper and lower critical temperatures increases, as does also the alcohol content of the solution. However, Snell (J. Phys. Chem., 1898, *2*, 457) showed that a solution containing 16.8% carbonate, 16.8% alcohol, and 66.4% water had a lower critical solution temperature of 40° and an upper one of 70°. This is very close to the plait-point as given by Cuno (30 gms. alcohol, 22.5 gms. carbonate, and 100 gms. water, or 14.75% carbonate) and would tend to throw doubt on the latter's statement. These determinations have been plotted in Figure 13, the two temperatures at which the solution just clears being joined. The plait-point is also indicated, and the apparent locus of the upper critical temperature for solutions having a lower critical temperature of 25°.

In Figure 14 will be found plotted the results we obtained for points on the isotherms at temperatures of 7.6 and 13.6°, and the general course of the isotherm for 25°. This was the upper one of a pair of conjugate solutions, and the isotherms therefore represent upper critical temperatures.

In the system: potassium fluoride, ethyl alcohol, water, no previous work has been done. Qualitative determinations which we have made indicate that the isotherms lie very close together, and the influence of temperature upon the binodal curve is small. Several homogeneous solutions were heated nearly to boiling and cooled in a freezing mixture without noticeable clouding, while one or two showed a trace of separation.

In the system: potassium carbonate, methyl alcohol, water, B. de Bruyn, (Z. Phys. Chem., *32*, 63) by determining the location of the quadruple point (vapor, two liquids, hydrate) at various temperatures, has concluded that as the temperature is lowered, the composition of the two liquid layers at the quadruple point becomes more nearly alike, until at about −35°, they become identical, hence below this temperature the liquid can exist in but one phase, *i. e.*, this is the lower limit of the lower critical solution temperature. He does not find that the isotherms in this system cross at all. It thus appears that the crossing of the isotherms at the plait-point is not a necessary condition in all systems.

The three systems involving propyl alcohol have never been studied before, and it was here that the influence of the temperature appeared to be the greatest. In the system containing potassium fluoride, at a content of about 21 gms. per 100 gms. solvent, cooling the solution from 25.6 to −3° increased the amount of propyl alcohol dissolved from 2.57 to 3.35 gms. per 100 gms. solvent. Points on the isotherms for several different temperatures were determined, and are plotted in Figure 15. In the same system, with a solution near the alcoholic end of the binodal curve (fluoride 0.533, water 29.93 and propyl alcohol 70.07 gms. per 100 gms. solvent) a lower critical solution temperature of 27° and an upper one of 41.5° could be clearly found.

In the system: potassium carbonate, propyl alcohol, water, an attempt was made to determine the effect of temperature changes on the solubility of the alcohol in solutions having a constant salt content. One of the solutions left from a determintion of the binodal curve was taken, its upper and lower critical solution temperatures determined, and an aqueous carbonate solution of the same strength made up. Small weighed portions of the latter were added, and the critical solution temperatures determined. The results are plotted on Figure 16. In an attempt to get another similar but more extended curve, more salt was added, the solution cooled to −12°, and water added in small portions with shaking. As the water warmed the solution, it was cooled after each addition, but it was noticed at one point, that the addition of the water partly cleared up the solution, but the cooling clouded it again. Suspecting the presence of another upper critical temperature, the solution was removed from the freezing mixture, and allowed to warm up. At −10° the solution cleared completely, but cooling for a fraction of a degree produced copious cloudiness. Careful examination failed to discover any separation of solid, so this appears to be a genuine upper critical temperature. On warming this solution to 60°, no separation was found. Upon now cooling to 25°, over 18 gms. of the alcohol had to be added to produce a separation into layers, showing that in this case the solution was unsaturated with respect to propyl alcohol at room temperature. As a matter of fact, comparison with the binodal curve showed the solution to contain 5% less alcohol than was required to saturate it at 25°. This solution, after adding the above-mentioned quantity of alcohol, was found to have a lower critical solution temperature of 23.5°, and an upper critical temperature of 57.6°. Upon now cooling below the lower critical solution temperature, a second upper critical solution temperature was found in exactly the same place as before, *viz.*, 10°. This is entirely out of harmony with the theory thus far developed, and it seemed best to leave this work to be continued later after procuring a supply of purer alcohol, so that the influence of any possible impurities might be eliminated. These results have also been plotted in Figure 16.

The influence of temperature upon the equilibrium in the case of propyl alcohol and sodium chloride is larger than in any other case here studied. A series of points on isotherms for various temperatures were determined and are plotted with the binodal curve in Figure 11. The course of the isotherms at these temperatures is indicated in Figure 17.

Some experiments were also performed with solutions containing more alcohol and less salt, both upper and lower critical solution temperatures being obtained. After making corrections for the variation of the salt content, the results plotted in Figure 18 were obtained. This represents graphically the influence of temperature on the solubility of the alcohol in solutions of a constant salt content (2.280 gms. per 100 gms. solvent). Here as in the system: potassium carbonate, propyl alcohol, water, some of the upper isotherms coincide with some of the lower ones.

SUMMARY

Six ternary systems of the class salt-alcohol-water have been investigated, and the complete curves for each worked out and drawn. In those which involve hydrated salts it is shown that the solubility of the salt is greater in absolute alcohol than when the alcohol is diluted with a small amount of water: in general, the solubility is about the same in absolute alcohol as in 60-70% alcohol.

A new method for the determination of ethyl alcohol has been worked out, and the results indicate that it is accurate in the presence of a small amount of methyl alcohol, if properly conducted.

It is shown for the first time that potassium fluoride has a very strong salting-out power for alcohols, and that its saturated solution is a better drying agent than a saturated solution of potassium carbonate, as it has a lower vapor pressure. The anhydrous salt itself is a good dehydrating agent, and more rapid than potassium carbonate on account of its greater solubility in organic liquids, at least in the alcohols here studied. It is also unique among drying agents of its class in the large per cent of water it will take up, to form the lowest hydrate.

A few experiments on the effect of temperature changes on the position of the binodal curve in the systems studied, show this influence to be very varying in quantity. Both upper and lower critical solution temperatures were obtained in the same solution in several cases, and apparently in one of the systems there exists a second upper critical temperature below the lower critical temperature.

ON THE POLYMERIZATION OF LIQUIDS AND A GENERAL METHOD FOR DETERMINING ITS RELATIVE VALUE

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In a recent paper[1] presented before the Royal Society of Canada at its May meeting, 1912, I applied a new molecular thermodynamic theorem to test, theoretically, the degree of polymerization of liquid substances. The dynamic basis of the theorem independently of its thermodynamic implications, may be concisely stated as follows:

The attractive forces which maintain a substance in the free liquid phase are just numerically equal to the pressure the same substance would exert, were it a perfect gas, at the same temperature and density.

The thermodynamic significance of this theorem lies in its furnishing the force function which may be applied in all isothermal changes of phase between liquid and vapor. From the fundamental equation for work, $W = \int_1^2 F\,ds$, we may always, theoretically, find the heat equivalent of the work when F can be expressed as a function of s, the displacement. When this function is expressed in terms of pressure and volume the above theorem leads directly to the conclusion that $\int_1^2 P dv = k \int_1^2 \frac{dv}{v}$, which follows because it implies that the force, whether attractive, or exerting a pressure, is always proportional to the number of molecules acting on or through unit area. If we ignore the difference in sign, which alone distinguishes an attraction from a pressure, the force function is the same as that of the pressure exerted by a perfect gas. A number of experimental facts and theoretical reasons were advanced to establish the validity of the theoretical applications made. For details the former papers (*loc. cit.*) may be consulted.

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[1] Jour. Phys. Chem. *16*, 455 (1912).

However, there is another aspect of the theorem to which attention never has been directed, so far as the writer is aware; but as it has special significance in connection with polymerization as the fundamental source of liquid stability it should be considered in connection with estimates of the degree of polymerization.

POLYMERIZATION AND LIQUID STABILITY

Probably the first impression made on most minds by the bare statement of the equality of the attractive and pressure relation of molecules contained in the above dynamical theorem is one of *instability*. If the forces are so delicately balanced whence comes the liquid stability with which we are all familiar? Why should the forces be just equal and not more or less? In a vague sort of way the molecules are generally regarded as held by some powerful attraction represented by thousands of atmospheres. It is perfectly evident on reflection that the whole attraction cannot exceed the sum of its parts or, that the attraction per unit area cannot exceed the sum of the pressures of the separate molecules acting in *one* direction through any element of area. The tension in a spring is measured by the pull on *one* end not by the sum of the pulls on the two ends. Likewise the force should be measured by the rate of change of momentum *normal to one side* of an element of area. This is what we call pressure and is what we should regard as the attraction also, since it is just sufficient to neutralize any pressure in the opposite direction. This view leads to the preceding theorem. The mathematically inclined may also doubtless reach the same conclusion through the application of D'Alembert's principle to a moving system of molecules.

THE SOURCE OF LIQUID STABILITY

Since the molecular forces in a free liquid must be in a state of equilibrium and the molecules are all relatively in motion with the same average speed of translation that they would have at that temperature were they perfectly gaseous, it is at once obvious that any *greater* force than that specified in the theorem would drive at least some of the molecules into contact, or union, and thus destroy their *relatively free motion.* It is also obvious that any *less* attractive force than that just sufficient to hold the molecules at the proper average distance would allow at least some molecules to escape and thus *cool* the remaining liquid. Let us call the union of two or more exactly similar molecules to form one, polymerization and the heat given out by the union, the heat of polymerization. (Since by Maxwell's law the average kinetic energy of translation is independent of the mass, such union must either increase the average *energy per molecule* of the system, or the system must give out heat.) With this in mind the part played by the polymerization in producing stability in the phase equilibrium is manifest. The union, or coalescence, of molecules must *raise* the average temperature of the remaining molecules and the escape of free vapor molecules must *lower* the average temperature by permitting additional molecules to de-polymerize. In consequence of this relation of polymerization to heat, the *stability of the system of balanced* forces which would otherwise be unstable, is maintained, so that the actual number of molecules can be disturbed, or changed, only by a transfer of energy in the form of heat or work, to or from the liquid. *The polymerization thus performs the function of a "source and sink" of heat energy and renders possible a stable equilibrium of freely moving independent molecules acted on by attractive forces,* without the intervention of any hypothetical repulsion.

RESOLUTION OF THE HEAT OF VAPORIZATION INTO COMPONENTS

During an isothermal change of phase from the vapor to the liquid phase, heat must be removed from the system of molecules in order to permit of the change. This heat, as we have seen, must consist of two parts, *first*—the heat of polymerization due to the decrease in the number of molecules, and *secondly*—the heat equivalent of the work due to all the forces acting during the process. It is easily seen that these two separate sources of the heat of vaporization, L, may be regarded separately and treated as independent of each other provided we are able to estimate the work due to the forces concerned. This we are able to do in the case of isothermal processes, by applying the theorem previously given, since the force at any instant depends upon the number of free molecules independent of polymerization. (The "force" is to be understood as independent of whether due to an external pressure or internal attraction.) Suppose we have N molecules occupying a volume V at a temperature T. Now suppose the volume to be decreased isothermally during which the heat L is given out and the combined external and internal forces do the amount of work W and the number of molecules is diminished by an amount n, the n molecules uniting with others, so that the number becomes $N{-}n$. From Maxwell's law and the principle of conservation, using the same units for heat and work:

$$W+\tfrac{1}{2}Nm_1u_1^2=L+\tfrac{1}{2}\,(N-n)\,m_2u_2^2$$

where L is the heat given out during the isothermal process. By Maxwell's law $\frac{1}{2}m_1u_1^2=\frac{1}{2}m_2u_2^2=\frac{1}{2}m\,u^2$, therefore

$$L-W=\tfrac{1}{2}n\,m\,u^2=H,\text{ or }L=W+H$$

where H is the heat of polymerization due to the decrease in the number of molecules occurring during the isothermal change from a vapor to a liquid.

A General Method of Finding the Relative Polymerization of two Liquids

At the time the previous paper was written it was not possible for me to do more than to show that all the liquids examined (many of which are regarded as non-associated,[1] or as consisting of simple vapor molecules) are according to the present theory, considerably polymerized. For the details of the theory and method of computation the former paper may be consulted. The quantities H and W and the ratio $r=\dfrac{L}{W}$ were found for thirteen different liquids of various different chemical types, but except in the case of water no estimate of the ratio of the weight of the liquid to the vapor molecule could be made, for no method of general application for such purpose had been found. Since then, however, further study of the subject has shown how the theory may be applied and used to determine the relative molecular weights of the liquid and vapor phases of any *other* liquid substance when these values are known for any *one* substance which may be used as a standard of comparison. In the case of water, as previously mentioned, it was possible, from certain available experimental data, to make a fair estimate of the relative molecular weights of the liquid and the vapor as lying between 2.5 and 1.9 at 0°C. The minimum value, 1.9 at 0°C., agrees with the value found by van der Waals[1] from entirely different considerations. In an early paper, W. Ramsay and J. Shields,[2] from surface tension experiments, found a value lying between 3 and 4; but in a later paper, Dr. Ramsay[3] reduced this estimate to 1.707 for water at 0°C.

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[1] Nernst. *Theoretische Chemie.* 6te *Auf.* 282 (1909).

For the present paper the polymerization of water has been computed and tabulated at intervals of 20° from 0° to 200°C., and will be used later as a standard of comparison in computing the relative polymerization of the remaining dozen liquids discussed in the previous paper. The method will be found to be a perfectly general one and is not necessarily confined to the use of water as a standard. When any other substance becomes better known than water it may be used instead of water.

Let us consider any two substances S_1 and S_2 of which the molecular weights as vapor and also the values L and W previously explained, are known. Let m represent the molecular weight of the vapor and m' the molecular weight of the liquid, H_1 and H_2 the heats of polymerization, where $H=L-W$. The values L and H refer to one gram of the substance. Hm will then represent the heat of polymerization of a gram mol and must be proportional to the number of molecules that unite with others to form complex ones. Hence we have generally

$$\frac{H_1m_1}{H_2m_2}=\frac{n_1}{n_2} \tag{A}$$

The quantity we wish to find is $\frac{m'}{m}$ which for brevity will be written x.

Since the total mass of n molecules is unchanged by polymerization we must have in the two cases

$$n\,m_1=n'_1m'_1 \text{ and } n\,m_2=n'_2m'_2$$

where n' represents the number of molecules of liquid. But

$$n-n_1=n'_1 \text{ and } n-n_2=n'_2$$

hence

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[1] Zeit. phys. Chem. *13*, 715 (1894).
[2] Zeit. phys. Chem. *12*, 433 (1893).
[3] Zeit. phys. Chem. *15*, 115 (1894).

$$n=(n-n'_1)\frac{m'_1}{m_1}=(n-n_2)\frac{m'_2}{m_2}$$

By substitution and elimination we get finally

$$\frac{H_1m_1}{H_2m_2}=\frac{\frac{x_1-1}{x_1}}{\frac{x_2-1}{x_2}} \qquad \text{(B)}$$

where all the quantities are supposed to be known except x_2, that is, the ratio of the weight of the liquid to the vapor molecule of the substance investigated at the specified temperature, the value of x_2, however, depending upon the value x_1, of the liquid supposed known.

The method of finding the value of x for water was given in detail in the former paper (*loc. cit.*) and need not be repeated here. The above method to be strictly applicable must be used for the same temperatures. Hence the value of $x=\frac{m'}{m}$ for water was first found for each 20° from 0° to 200°C. and tabulated in the accompanying Table I. The value of L at the different temperatures was found by applying Clausius' formula $L=607-.7t$ as being sufficiently accurate although it probably is not very reliable for high temperatures. The specific volumes for liquid and vapor water (saturated vapor) were taken from Winkelmann,[1] Matthiessen's values for the liquid being used from 0° to 100° and the table of Waterston for values from 100° to 200°. Battelli's values of the specific volumes of the vapor were used except for the temperature 160° which was omitted. The value 307.3 was taken from the table of Knoblauch, Linde and Klebe (p. 997). The remaining values are taken from the author's previous paper.

The value of L for most substances are most accurately known at their normal boiling points; hence it is desirable to have a standard liquid covering a wide range of temperatures. Hence the utility of the water table. From the degree of accuracy at present possible it was deemed sufficient to use 20° intervals in the construction of the table. The entire data are given in the table in order that the theory and results may be conveniently checked by those interested.

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[1] Winkelmann, *Handbuch d. Physik* III, pp. 92–94, 996, 997.

TABLE I

POLYMERIZATION OF WATER, $\frac{m'}{m}$ (WITH DATA)

Temp.	Specific Volumes		Calories			
C.	Liquid	Vapor	L	W	H	$\frac{m'}{m}=x$
0		204000	607	365.6	241.4	2.11
20	1.0018	57730	593	351.7	241.3	2.02
40	1.0077	19484	579	338.2	240.8	1.93
60	1.0170	7650	565	325.5	239.5	1.86
80	1.0290	3401	551	313.3	237.7	1.80
100	1.0432	1667	537	301.5	235.5	1.75
120	1.0600	893.1	523	290.0	233.0	1.70
140	1.0795	511.4	509	278.6	230.4	1.63
160	1.1015	307.3	485	266.0	219.	1.58
180	1.1268	197.1	471	256.2	214.8	1.54
200	1.1578	130.6	457	244.8	212.2	1.51

Two illustrative examples of the method of computation will be given in some detail, and the results of the computation of the remaining twelve substances will be found in the column $\frac{m'}{m}$. The data for the computations are included in the table under appropriate column headings.

Attention was called in the previous paper to the necessity of taking into account possible polymerization of the vapor when determining the value of $H=L-W$ as the result gives only the *change* in the polymerization; but in the case of acetic acid I failed to profit by my own warning and used the theoretical molecular weight 60 instead of the actual which is about 97 according to its vapor density. The result was a value much too low and is corrected in the present table.

The following table gives data and values of $\frac{m'}{m}$ for all the substances for which I could obtain the necessary experimental data.

TABLE II

Substance	Temp.	Calories			Mol.	$\frac{m'}{m}$
	C.	*L*	*W*	*H*	Wt.	
Benzene	80	93.5	51.3	42.2	77.4	1.51
Carbon tetrachloride	20	51.1	28.6	22.5	153.7	1.61
Carbon tetrachloride	77	44.3	25.1	19.2	153.7	1.42
Carbon bisulphide	20	88.0	52.9	35.1	75.5	1.40
Ethyl ether	35	90.	44.3	45.7	73.6	1.59
Methyl formate	31.8	110	60.4	49.6	59.6	1.52
Methyl propionate	79.7	89	44.3	44.7	87.4	1.66
Ethyl acetate	77.	92.7	43.9	48.8	87.4	1.75
Propyl acetate	140	83.2	39.4	43.8	101.3	1.71
Methyl alcohol	66	262.0	134.0	128.0	31.8	1.78
Ethyl alcohol	78.4	216.4	91.5	124.9	46.	2.48
Propyl alcohol	97.4	166.3	71.8	94.5	60.	2.35
Acetic acid	118	97.	47.2	49.8	97.	1.905
Water	0	606.5	363.	240.5	18.	2.11
Water	100	537	300	237.	——	1.75

Let us take ethyl alcohol as the first example. Its boiling point 78° is near enough to 80° to allow us to use the data of water at 80°. Taking the necessary data from the tables we have for alcohol at 78°

$$\frac{H_1 m_1}{H_2 m_2} = \frac{\frac{x_1-1}{x_1}}{\frac{x_2-1}{x_2}} \qquad \frac{237.7\times 18}{125\times 46} = .744 = \frac{.444}{\frac{x_2-1}{x_2}} \therefore x_2 = 2.48$$

For acetic acid at 118° we may use water at 120°

$$\frac{233\times18}{49.8\times97}=.868=\frac{.412}{\frac{x_2-1}{x_2}}\ \therefore\ x_2=1.9$$

In this case since the vapor was already 1.6×60 and underwent a further increase of 1.9 the total increase or actual liquid molecule is $1.6\times1.9=3.1$.

CONCLUSION

Particular attention is called to the functional part played by polymerization in maintaining equilibrium stability. The current impression that there exist immense internal pressures in liquids may conveniently be abandoned. They are dynamically impossible and otherwise serve no useful purpose. Unless we abandon entirely the Newtonian mechanics and the principle of D'Alembert the inwardly directed pressure cannot exceed the outwardly directed reaction, in a system of freely moving particles.

A very obvious objection that will no doubt be made at once by some physical chemists is, that the assumption of the perfect gas law as the law of force is unverifiable by experiment and is "too theoretical." The first reply to this objection should be that "the perfect gas law" actually assumed is entirely different from assuming that a given substance acts like a perfect gas or that it may be treated as a perfect gas because the internal attractions are negligible. The fundamental assumption that *is* made is one that is supported by the universally accepted principles of dynamics; and that is that the force of attraction which diminishes a pressure must be numerically equal, but opposite in sign, to the diminution in pressure produced by it. The *direction of the action* can have no influence on the *magnitude* of the work performed by it. So far as work is concerned it is immaterial whether it be done by a push or a pull or by a combined push and pull; and if the only effect of a pull is to diminish the push required and we know how much push would be required if there were no pull, then we may assume all push or all pull at pleasure without affecting *the computed amount* of the work due to the forces concerned. *The heat equivalent of work done by forces is* *entirely independent of the nature of the body upon which the work is done.*

A second reply might be: Suppose we admit that the fundamental assumptions are erroneous. Then the difficulty would be to explain the remarkable consistency of the results obtained and the practical agreement in many ways with the best results obtained by other methods. The values obtained for water are, of course, only a first approximation, but the *relative values* obtained, also depend upon the theoretically determined heat of polymerization. This is the fundamental basis of the whole theory; and the remarkable consistency of the results obtained would be even more wonderful considered as a system of accidentally balanced errors than as the "workings of a law of Nature."

THE RELATION BETWEEN THE POTENTIAL OF LIQUID AMALGAM CELLS AND THE CONSTITUTION OF THE AMALGAM

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In 1891 G. Meyer published his well-known research[1] on the molecular weights of certain metals as determined by the potential of amalgam cells, drawing the conclusion that the metals investigated dissolved in mercury as atoms. In 1902 Haber[2] called attention to the fact that Meyer's measurements do not decide between the case of a metal dissolved in mercury as single atoms and that of a hydrargyrate of the composition MHg_m. By calculating the osmotic work necessary to transfer the solute from one amalgam to the other on the assumption of a hydrargyrate being formed, he showed how the ordinary formula must be modified, and calculated the extent of the effect on the potential. However, as the amalgams become more concentrated an additional and uncertain cause of deviation arises in the inexactness of the gas-laws as applied to osmotic pressure except at great dilution. Hence it is unsafe to refer to the formation of hydrargyrates all deviations from the simple concentration formula,

$$nEF = RT\ 1n\frac{c_1}{c^1_2}.$$

Haber proceeds to show that an exact expression can be given only in terms of vapor pressure, and, by analogy with the equation applied by Dolezalek[3] to the lead accumulator, gives the equation,

$$nEF = RT\left(w_2 \ln p_2 - w_1 \ln p_1 - \int_{w_1}^{w_2} \ln p\, dw + m \ln\frac{p_2}{p_1}\right)$$

In this expression n denotes the valence of the dissolved metal, E, the e.m.f.; F the Faraday equivalent, R the gas-constant,

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[1] Zeit. phys. Chem. *7*, 477 (1891).
[2] Ibid. *41*, 399 (1902).
[3] Zeit. f. Elektrochem. *4*, 349 (1898).

T the absolute temperature, w the number of mols of solvent mercury per mol of solute, p the pressure of mercury vapor over the amalgams, and m the number of atoms of mercury combined with one atom of the solute metal. The subscripts, 1 and 2 refer to the concentrated and dilute amalgams respectively.

Now, it would appear from this equation that if p were known as a function of w the expression could be integrated and the value of m determined which would satisfy measured values of E. The question of solvation would be thus settled beyond the shadow of a doubt. A closer examination of the equation, however, shows that the value of m cannot be so determined, and that a method so free from objection for the determination of solvation is not involved in the equation.

If N denotes the number of mols of mercury present, including both solvent and solvate mercury, then, since

$$N_1 = w_1 + m, \text{ and } N_2 = w_2 + m,$$

the equation becomes,

$$nEF = RT(N_2 \ln p_2 - N_1 \ln p_1 - \int_{N_1}^{N_2} \ln p dN).$$

This will be more evident if the expression is derived directly, by a process of isothermal distillation.

Let us imagine two large reservoirs containing concentrated and dilute amalgams, I and II, respectively. We can transfer one atom of the solute metal, M, from I to II electrically, as in a concentration cell, whereby the work nEF would be gained. The same transfer may be made by isothermal distillation as follows.

1. Remove from I 1 mol MHg_m together with the corresponding solvent mercury, $N_1 - m$ mols. This requires no work.

2. Distill into this portion from II enough mercury vapor to bring it to the same concentration as the amalgam in II. The amount distilled is $(N_2 - m) - (N_1 - m)$, or, $N_2 - N_1$, and the work done is

$$RT \int_{N_1}^{N_2} \ln \frac{p_2}{p} dN.$$

3. The separated portion is now of the same concentration as the amalgam in II and is added to it without doing any work.

4. We have now transfered from I to II $N_1 - m$ mols of solvent mercury and m of combined mercury, or N_1 mols altogether, in addition to 1 mol of the metal M. To make the process equivalent to the electrical transfer, we have finally to distill back into reservoir I N_1 mols of mercury, doing the work,

$$N_1 RT \ln \frac{p_2}{p_1}$$

Equating the total work done in the distillation process to the electrical work, we have,

$$nEF = RT\left(N_1 \ln \frac{p_2}{p_1} + \int_{N_1}^{N_2} \ln \frac{p_2}{p} dN\right) = RT\left(N_2 \ln p_2 - N_1 \ln p_1 - \int_{N_1}^{N_2} \ln p dN\right).$$

It will be noticed that wherever m occurs it cancels out, and so does not appear in the final equation.

Now, this expression can be still further simplified by putting

$$\int \ln p dN = N \ln p - \int N d \ln p.$$

whence we obtain as the final form,

$$nEF = RT \int_{N_1}^{N_2} N d \ln p; \text{ or } nEF = RT \int_{N_1}^{N_2} \frac{N dp}{p}.$$

It must not be inferred from this that the potential of amalgam cells should be unaffected by the formation of hydrargyrates, for though m does not appear in the equation as given it is involved in any expression giving p as a function of N which we may use to integrate the final equation for e.m.f. here given by the writer.

We will now show how this equation can be integrated using the vapor pressure law to take into account the constitution of the amalgams involved.

Very accurate measurements of the potentials of amalgam cells have been made in recent years in the Harvard[1] and Princeton[2] laboratories. These measurements have shown that the gas-laws hold accurately at high dilutions, but that considerable deviations occur at greater concentrations, the direction depending upon the solute metal. Thallium, indium and cadmium give potentials greater, and zinc, lead and tin smaller than those calculated from the simple concentration formula. A number of methods of accounting numerically for these differences are used by Richards and his co-workers, but while the energy changes are rather well accounted for thermodynamically, the effect of polymerization or solvation is merely considered qualitatively, and that chiefly in the case of zinc, showing in a general way that the deviations are in the direction expected.

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[1] Richards and Forbes, Pub. Carnegie Inst. No. 56, and Zeit. phys. Chem. *58*, 683 (1907). Richards, Wilson, and Garrod-Thomas, Pub. Carnegie Inst. No. 118, and Zeit. phys. Chem. 72, 129, 165 (1909).

[2] Hulett and DeLury, J. Am. Chem. Soc. 30, 1812 (1908). Crenshaw, J. phys. Chem. *14*, 158 (1910).

Let us suppose that the dissolved metal forms a solvate with the mercury of the general formula MHg_m. Then, if the solution is made from 1 mol of M and N mols of mercury, the solvent mercury would be $N-m$ mols, and the total number of mols would be $N-m+1$. Using these values for the mol-fraction of mercury in the vapor pressure law,[1] which states that the pressure of a component over of a mixture is proportional to its mol-fraction in the mixture, the proportionality constant being the saturation pressure of the pure component p_o, we get the equation,

$$p = p_o \frac{N-m}{N-m+1}.$$

If this function of p in terms of N is used to integrate the general formula deduced above, the resulting equation is

$$E = \frac{2.3026RT}{nF}\left[m\log\frac{N_2-m}{N_1-m} - (m-1)\log\frac{N_2-m+1}{N_1-m+1}\right].$$

In applying this formula we will consider the case of thallium amalgams. Freezing point data have furnished definite evidence of the existence of the compound $TlHg_2$ in the solid state. In Table I are given the results of Richards and Wilson[2] on the potential of thallium amalgams at 30° compared with the results calculated from the ordinary concentration equation and from the equation just given, using for m the values X, 2, 5, and 6 successively. It will be seen that the value $m=2$ improves the agreement with the measured potentials considerably, a much better agreement is gotten from the value 5 or 6.

We must conclude from this that dilute thallium amalgams contain the compound $TlHg_6$. It will be interesting to confirm this by means of measurements of vapor pressure of thallium amalgams.

[1] Cf. ~~preceding~~ paper.

[2] l.c. following

TABLE I

%Tl	N	Potential in millivolts at 30°				
		Observed	Calculated from			
			c/c^1	$TlHg_2$	$TlHg_5$	$TlHg_6$
1.8456	54.2					
		37.13	32.78	34.42	36.60	37.42
0.5249	193.5					
		22.61	21.61	21.90	22.32	22.52
0.2294	443.5					

Let us now apply to the fundamental equation for e.m.f. the vapor pressure measurements made by the writer[1] on zinc amalgams. It has been shown that the vapor pressures of zinc amalgams are given quite accurately by the equation,

$$\frac{p}{p_o}=\frac{2N(K+4)}{N(K+8)+K+4+\sqrt{(KN+K)^2+4K(2N+1)}},$$

where K is the equilibrium constant of the reaction,

$$2Zn=Zn_2,$$

as given by the equation,

$$\left(\frac{1-2\alpha}{N+1-\alpha}\right)^2=K\frac{\alpha}{N+1-\alpha},$$

in which α represents the number of mols of Zn_2 produced. α is gotten in terms of K and substituted in the vapor pressure law which, in this case, is expressed as

$$\frac{p}{p_o}=\frac{N}{N+1-\alpha},$$

In order to integrate the expression

$$nEF=RT\int_{N_1}^{N_2}Ndlup$$

we can write, since α is small when N is large, a condition fulfilled in the e.m.f. measurements we shall use,

$$\frac{I}{N}=K\alpha.$$

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[1]Cf. ~~preceding~~ paper.
following

If the value $K=0.50$ holds at lower temperatures than

$$\frac{p}{p_o}=\frac{N}{N+1-\frac{2}{N}},$$

and

$$\frac{p}{p_o}=\frac{N^2}{N^2+N-2}.$$

Using this equation in the above integration, we get for the e.m.f. of zinc amalgams

$$E=\frac{2.3026\,RT}{2F}\left(2\log\frac{N_2+2}{N_1+2}-\log\frac{N_2-1}{N_1-1}\right)$$

To test this equation we have both the measurements of Richards and his co-workers[1] and those of Crenshaw.[1] Table II gives observations of Richards and Garrod-Thomas on the potential of the most concentrated amalgams used. Compared with the observed values are given those calculated from the ratio c_1/c_2 and from the equation just derived by the writer.

In Table III are given similar figures for the amalgams measured by Crenshaw, which extend to much higher concentrations, where the deviations from the gas-law equation are very great. Here again, however, the potentials calculated from p are in excellent agreement with the observed potentials, the slight deviations being in the direction produced by the simplifying assumptions made in integration.

It may seem strange that the value of K obtained at 300° should apparently remain the same at ordinary temperatures. It is by no means impossible, even though somewhat unusual. The constancy of K is borne out in a rather imperfect way by the vapor pressure measurements. The ration p/p_o seemed to be independent of temperature, although careful measurements of this ratio at a widely differing temperature have not yet been made.

It must be emphasized, finally, that even though it were shown that the experimental values of the relation between p and N are not due to association of zinc atoms, nevertheless, the course of the vapor pressure curve, and therefore the potentials calculated from it, remain the same, and therefore in agreement.

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[1] l.c.

It may be concluded, therefore, that the equation here given by the writer is confirmed by the behavior of zinc, and the probable behavior of thallium amalgams. The writer hopes soon to be able to report measurements upon thallium and other amalgams.

TABLE II

%Zn	N	Potential in milli-volts. 30°		
		Observed	Calculated from	
			p	c_1/c_2
0.900	36.0			
		10.18	10.18	11.13
0.384	84.9			
		6.12	6.18	6.45
0.234	139.4			

TABLE III

$\frac{\text{grams Zn}}{\text{grams Hg}}$	N	Potential in milli-volts. 25°		
		Observed	Calculated from	
			p	c_1/c_2
2.20/100	14.86			
		0.89	0.87	1.34
2.00/100	16.36			
		0.94	0.98	1.35
1.8/100	18.17			
		2.43	2.48	3.23
1.4/100	23.35			
		3.54	3.57	4.32
1/100	32.70			
		7.83	7.93	8.90
5/1000	65.37			

THE VAPOR PRESSURE OF ZINC AMALGAMS

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Among the greatest triumphs of modern science must be reckoned the discovery and application of the laws governing dilute solutions, which may be grouped under the general idea of the application to solutions of the Rule of Avogadro. In all the development of chemistry there have probably been no principles which have proved to be such valuable instruments in the hands of investigators. However, the increasing deviations from these laws shown as solutions approach ordinary concentrations have produced the conviction that Avogadro's Rule as applied to solutions must be regarded as an extrapolation, and that a more exact law, applicable to concentrated solutions, must be established. The Law of Raoult for the lowering of vapor pressure, announced from a purely empirical basis, has more recently received the theoretical foundation and experimental proof which indicate that it is probably the nearest approach that we possess to an exact law of a perfect solution.

The problem has been clearly stated and its solution indicated by Nernst where he states,[1] "wir dürfen die aktive Masse des Lösungsmittels proportional der Koncentration des von ihm entsandten Dampfes setzen. . . . Dies Resultat wäre durch kinetische Betrachtungen nicht zu erhalten gewesen und ist auch erst von mir auf diesem Wege gefunden worden. Die Thermodynamik vermag uns also herin weiter zu führen, und es sei betont, dass bei der Behandlung konzentrierter Reaktionsgemische sie allein gegenwärtig die theoretische Führung zu übernehmen im stande ist, wären wir im Besitze von Regeln über die Dampfdrucke beliebig konzentrierter Gemische, so würden wir die Reaktionen solcher Systeme mit der gleichen Vollständigkeit behandeln können wie diejenigen verdünnter Lösungen." The vapor pressure of one component of a mixture is thus the direct measure of the "active mass" of the component in the mixture. The experi-

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[1] Theoretische Chemie, 5th ed., p. 647.

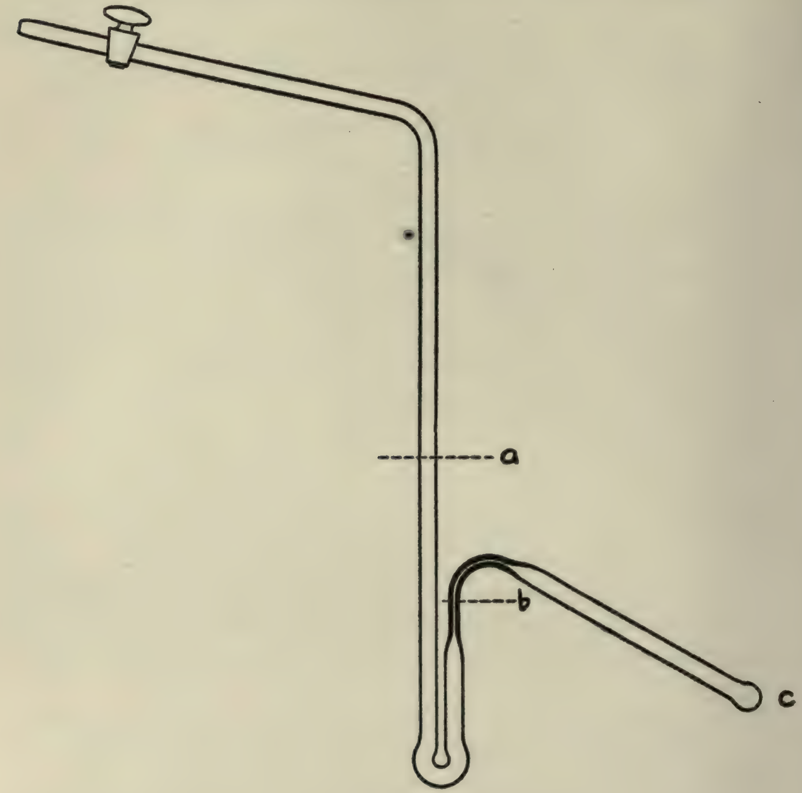

Figure 1

mental advantage of referring active mass to vapor pressure rather than to osmotic pressure, for example, is obvious.

Now, the other side of the equation involves the expression of active mass in terms of the quantities of material present. This seems possible by following the suggestion originally made by Gibbs, and advocated since by Plank, van Laar and others, that the active mass of a component of a phase is proportional to its mol-fraction, *i.e.*, to the number of mols of the component divided by the total number of mols present. Combining this with the above expression of Nernst, we have the law that *the vapor pressure of a component of a mixture is proportional to its mol-fraction.*

The constant of proportionality is given by making the mol-fraction 1, which shows it to be the vapor pressure of the substance in the pure state, that is, of the saturated vapor. The value of this law has been emphasized by a number of authors recently, among whom may be mentioned Dolezalek,[1] Lewis,[2] Möller,[3] and Washburn.[4] The interesting results of Dolezalek in determining the constitution of liquid mixtures and the importance of a reliable method of investigating the various problems of association, dissociation, and solvation, make, as Washburn says, the gathering of data along this line of great importance.

This study of the vapor pressure of amalgams was begun with the double purpose of testing the vapor pressure law upon solutions differing widely in physical nature from the organic mixtures to which it has hitherto been applied, and also of attacking the general problem of metal compounds from a new standpoint.

While the compounds of the metals with one another have been largely investigated in recent years by thermal analysis, the results so obtained allow nothing but inference concerning the nature of the liquid phase. The well-defined and varying physical constants of the metals promise much of interest as a result of a thorough study of their solutions in one another. The natural starting point of such a series of investigations is the amalgams, since they are liquid at not too extreme temperatures, and have measurable vapor pressures, allowing, therefore, their investigation by means of the vapor pressure law. The published work in this direction is very limited. The existence of hydrargyrates in solution has been the subject mainly of speculation.[5] The vapor pressures of very dilute amalgams have been studied in the comprehensive work published by Ramsay[6] a number of years ago, but the molecular weight of the metals was the object in view, and no conclusions were drawn regarding possible solvation although such is clearly indicated in several cases.

In the light of what has been said it is evident that a further study of this problem using more concentrated solutions is of considerable importance. The results upon zinc amalgams here presented are the first of a series which the writer hopes to carry out.

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[1] Zeit. phys. Chem. *64*, 727 (1908); *71*, 191 (1910).

[2] Journ. Amer. Chem. Soc., *30*, 668 (1908).

[3] Zeit. phys. Chem. *65*, 226 (1909).

[4] Journ. Amer. Chem. Soc., *32*, 653 (1910).

[5] See Berthelot, Ann. Chim. phys. 5 *18*, 433. Haber, Zeit. anorg. Chem. *44*, 399 (1902); G. MacP. Smith, Zeit. anorg. Chem. *58*, 381 (1908).

[6] Journ. Chem. Soc. *55*, 521 (1889).

EXPERIMENTAL PART

1. *Materials Used*

The mercury used was first washed in the apparatus described by the writer,[1] and then distilled as prescribed by Hulett.[2] The zinc was "Baker's Analyzed," the analysis giving 0.05% of lead, 0.004% of iron, no arsenic, and a trace of cadmium. An analysis made to confirm these figures gave 0.04% lead and 0.001% of iron. These amounts were far too small to influence the results.

2. *Apparatus*

For the purpose of measuring the vapor pressure the amalgams were confined in tubes such as shown in Fig. 1. The internal of this tubing was about 7 mm., thus minimizing the effect of the surface tension of the amalgam. In the first experiments the part between *b* and *c* was lacking. The part from *a* around to *b* was blown separately and fused onto the upper part after putting into it a weighed piece of zinc, which had previously been moulded into thin sticks and scraped free from surface oxide. The tube containing the zinc was then exhausted and enough mercury admitted carefully from a supply poured in beyond the stopcock to furnish an amalgam sufficient to fill the closed limb of the U-tube and extend well around the bend. The quantity of mercury used was determined after the experiment by cutting at *a*, and weighing the U-tube with and without amalgam. The amount of zinc being known, the mercury was given by difference. Vacuum reductions were not made, as the corrections thus made would have been beyond the limits of accuracy otherwise attainable. The tube now containing the mercury and zinc was heated while still exhausted, whereby the zinc amalgamated with the mercury and at the same time the short limb was boiled free from residual gas. The tubes were drawn to a point at *b* so that a minute bubble of gas could be easily seen. In the later experiments with more concentrated amalgams, Nos. 29 to 32, it was found necessary, in order to avoid the presence of oxide, to fill the tubes

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[1] J. Amer. Chem. Soc. *31*, 933 (1909).
[2] Phys. Rev. *33*, 307 (1911).

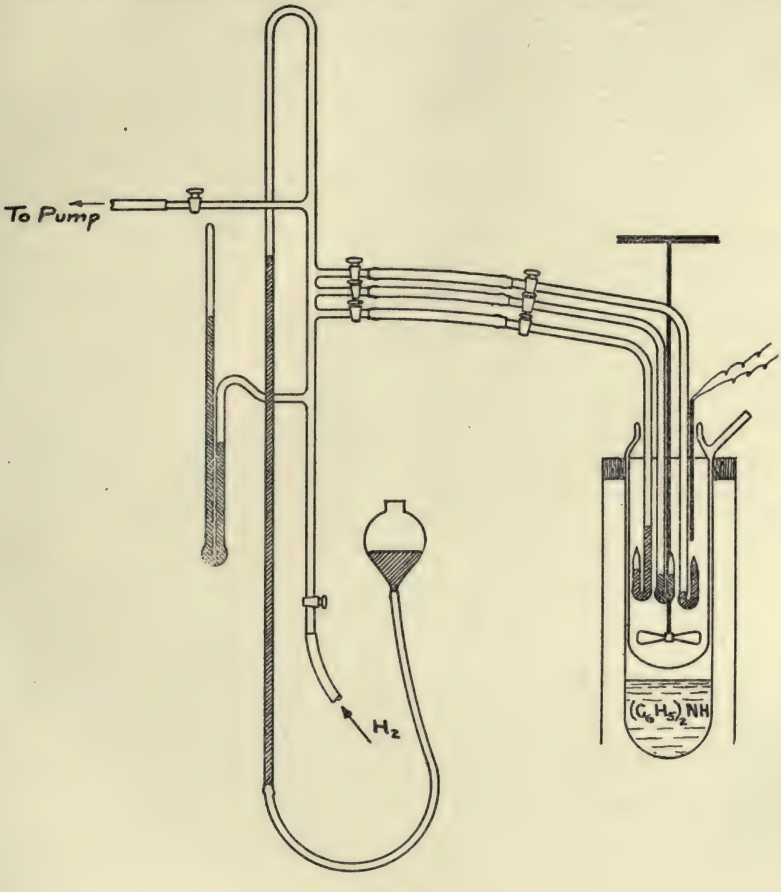

Figure 2

in a different manner. The tube was blown as shown in the figure except that it was left open at *c*. After introducing the weighed zinc at *c*, it was sealed at this point, the mercury introduced in a weighed amount at the other end, whereupon the tube was exhausted, filled with hydrogen and again exhausted. The mercury was then run into *b-c*, and hydrogen admitted to a pressure of slightly less than one atmosphere. On heating, the zinc amalgamated with the mercury and the amalgam was run through the capillary into the U leaving behind the small amounts of oxide which had collected on the surface. The capillary was sealed at *b*, leaving the tube ready for insertion into the thermostat. A similar tube containing mercury alone, and filled, of course, without the above precautions, served to give the vapor pressure of mercury for comparison.

The measurements were carried out at 300° in a thermostat shown in Fig. 2, and constructed for the writer by the Caloris Company of Philadelphia. It was constructed on the plan of a vacuum bottle, the outer bottle was elongated so as to contain the heating liquid, diphenylamine, whose vapors heated the liquid in the inner bottle. This latter was ordinary commercial "Cottolene." The side tube shown in the figure served as an air-condenser for the vapors of diphenylamine not condensed in the lower parts of the apparatus. The cottolene, protected from the air as much as possible by asbestos coverings, stood the high temperature fairly well. It gave off endurable quantities of acrolein and had to be replaced after two days' use on account of darkening. The apparatus was protected on the outside by a cylinder of glass cut from a tall beaker, and the space between the top of this cylinder and the bottle was closed by a roll of asbestos paper. The cottolene was stirred vigorously by a stirrer, as shown, run at a high speed by an electric motor. The temperature was determined by means of a copper-constantin thermocouple, the cold junction of which was kept in ice in a vacuum bottle. The e.m.f. of the couple was read on a Siemens-Halske galvanometer. The temperatures given later are, however, taken from the vapor pressure of the mercury as given by the careful measurements of Smith and Menzies.[1]

The vapor pressure of the mercury and amalgams at this temperature tends to make the liquid fall in the closed limb of the U-tubes, and this was balanced and measured with the aid of the connections shown in the left of Fig. 2. The tube containing the mercury and two containing amalgam were connected as illustrated, and the apparatus, including the rubber connections, pumped free from air. The cocks of the U-tubes were then opened and hydrogen, from a Kipp-generator, purified by passing over a heated copper spiral and drying with sulphuric acid, was admitted to a pressure sufficient, as the temperature of the thermostat rose to 300°, to keep the level of the amalgam in both limbs of one of the tubes approximately the same. Finer adjustment of pressure was made by means of the reservoir of mercury shown in the figure. This method of adjusting pressure seems easier than that used by Smith and Menzies.

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[1] J. Amer. Chem. Soc. *32*, 1434 (1910).

The pressure adjusted so that the mercury stood at the same level in one of the tubes, the greater pressure in the closed limb of the tube containing the pure mercury forced the mercury to rise in the other limb to an amount equal to the difference in pressure of the amalgam and of mercury. This difference in level was read by means of a cathetometer, simultaneous readings being taken on the manometer giving the pressure of the amalgam direct. A number of readings were taken with each tube, the pressure being readjusted before each reading. The pressure was also frequently increased to make sure of the absence of gas in the closed limbs. All readings were reduced to mm. of mercury at 0°. The readings on the cathetometer, being in mm. at 300°, were reduced by the factor 0.947, which is the ratio of the density of mercury at 300°, 12.881, to that at 0°, 13.596.

In experiments 29-32, the difference in pressure had become too great for the dimensions of the thermostat, also the mercury showed a tendency to boil in the open limb, so that a second apparatus similar to that shown on the left of the figure was used in connection with the U-tube of mercury. The mercury in this tube was now also adjusted to the same level and the pressure read independently on the attached manometer. The extra connections and the use of hydrogen were dispensed with in this part of the apparatus. This arrangement proved more satisfactory than the former where a cathetometer had to be used, and will doubtless be retained in future investigations.

3. *Results*

Table I gives a typical experiment, No. 31. In this, P_0 denotes the vapor pressure of mercury; P, that of the amalgam; N, the number of mols of mercury per mol of zinc. It will be seen that the slight changes in temperature affect the pressures in the same ratio, so that the simultaneous determination of the pressures made it useless to seek greater constancy in temperature.

Table II gives a summary of all the data secured, each line representing results similar to those of Table I. The values of the relative pressures, P/Po, are plotted in the curve, Fig. 3, against the atom-per cent of zinc, N/N+1, given in the fifth column of the table. If the amalgams were perfect solutions and obeyed the law $P/P_o = N/N+1$, then the graph should be a straight line, and the values in the sixth and seventh columns of the table should agree. It will be seen that the pressures are considerably higher than they should be for a simple solution.

TABLE I

Expr. No. 31. Wt.Zn = 6.712; Wt.Hg = 12.230

P	P_o	P/P_o	Temp.
111.9	241.8	0.463	299.4
108.9	240.8	0.453	299.0
112.4	241.3	0.466	299.1
111.9	241.3	0.464	299.1
108.9	237.8	0.458	298.5
109.9	238.8	0.460	298.7
110.9	240.8	0.461	299.0
111.9	241.3	0.463	299.1
112.9	242.1	0.466	299.5
		Mean 0.462	

TABLE II

No. of Expr.	No. of Observ.	%Zn	N	$\frac{1}{N+1}$	$\frac{N}{N+1}$	$\frac{P}{P_o}$	$\frac{N}{N+1-a}$	Δ
21	6	2.655	11.98	0.077	0.923	0.928	0.930	−0.002
8	9	3.72	8.461	0.107	0.893	0.906	0.906	+0.000
22	5	4.61	6.776	0.129	0.871	0.884	0.887	−0.003
6	10	5.74	5.353	0.158	0.842	0.854	0.863	−0.009
19	7	10.00	2.946	0.254	0.746	0.787	0.786	+0.001
12	6	10.63	2.747	0.267	0.733	0.771	0.774	−0.003
17	6	10.66	2.745	0.268	0.732	0.778	0.773	+0.005
20	5	11.75	2.458	0.290	0.710	0.743	0.756	−0.013
24	5	12.76	2.238	0.309	0.691	0.735	0.739	−0.004
18	4	13.74	2.056	0.328	0.672	0.718	0.725	−0.007
32	7	17.78	1.510	0.398	0.601	0.675	0.665	+0.010
25	8	19.52	1.348	0.426	0.574	0.658	0.642	+0.016
28	3	19.70	1.332	.429	0.571	0.644	0.638	+0.006
26	6	19.80	1.325	0.431	0.569	0.649	0.636	+0.013
30	5	26.00	0.929	0.519	0.481	0.561	0.559	+0.002
29	8	30.42	0.747	0.572	0.428	0.501	0.501	−0.006
31	9	35.45	0.595	0.627	0.373	0.462	0.454	+0.008

How can these deviations be accounted for? This was done by assuming, as Dolezalek has done, that the solute is associated to some extent, and hence the number of mols of zinc is less than is assumed in the simple formula.

Suppose that the atomic mols of zinc unite partially according to the equation,

$$2Zn = Zn_2.$$

If α represents the number of mols of Zn_2 formed from 1 mol of Zn, there would remain $1-2\alpha$ mols of Zn, and the total number of mols present in the mixture would be $N+1-\alpha$. Applying the law of mass-action, using mol-fractions instead of concentrations, we obtain the equation:

$$\left(\frac{1-2\alpha}{N+1-\alpha}\right)^2 = K\frac{\alpha}{N+1-\alpha}$$

Solving this equation for α, we get

$$\alpha = 0.5 + \frac{KN - \sqrt{(KN+K)^2 + 4K(2N+1)}}{2(K+4)}$$

(The minus sign before the radical is evidently correct.) Now, since the relative pressure should be equal to the mol-fraction of mercury:

$$\frac{P}{P_0} = \frac{N}{N+1-\alpha}$$

Substituting the above value of α in this equation we obtain:

$$\frac{P}{P_0} = \frac{2N(K+4)}{N(K+8)+K+4+\sqrt{(KN+K)^2+4K(2N+1)}}$$

The values given in the eighth column of Table III and represented by the curve in Fig. 3 were obtained by putting

$$K = 0.50,$$

when the equation becomes:

$$\frac{P}{P_0} = \frac{9N}{8.5N+4.5+\sqrt{0.25N^2+4.5N+2.25}}$$

The last column, Δ, in the table gives the differences between the observed values of P/P_0 and $N/N+1-\alpha$, calculated by this equation. The closeness with which the results agree is very striking, admits of hardly any other conclusion than that the assumptions involved are correct. If zinc is associated in solution in mercury, then the vapor pressure law expresses the behavior of the solution up practically to the limit of the solubility of zinc in mercury at this temperature.[1]

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[1] 70.5 atom per cent zinc, according to Puschin, Zeit. anorg. Chem. *36*, 201 (1903).

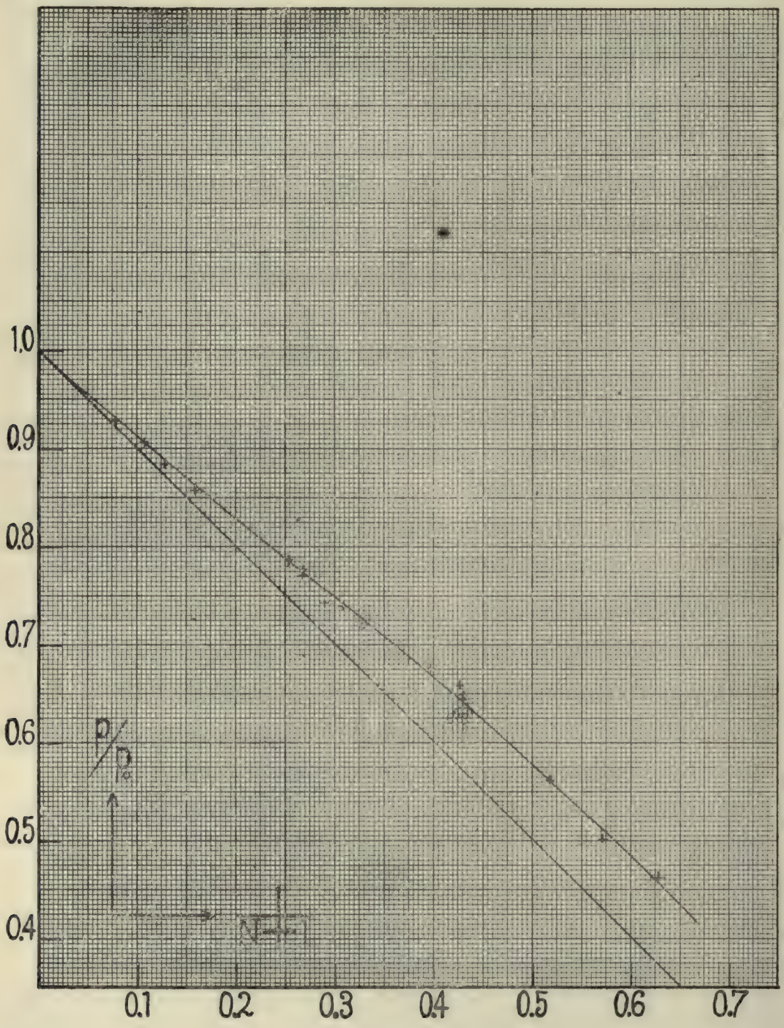

Figure 3

It is interesting, furthermore, to note the extent of the association at various concentrations, calculated from the value of K = 0.5,

N	100	10	1	0
Per cent association	4	22	52	66.7

If zinc could exist in the liquid state at 300° it would accordingly be $\frac{2}{3}$ associated to Zn_2.

CONTRIBUTIONS TO THE CHEMICAL KINETICS OF ENZYMES

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The gradual decay of the enzymes in the course of the reactions is one of the factors which make exact study of enzymatic actions so very difficult. For the further progress of this important branch of chemical kinetics, it is, therefore, necessary that this problem should be thoroughly investigated. In the following the results obtained on some special points of the subject are communicated.

As there is hardly any doubt that enzymes are of colloidal nature, the theoretical treatment would be hopelessly complicated if the cases were studied in which the substrata are also colloids. Hence the present investigation is limited to the cases where the substrata form genuine solutions.

As enzymes are known at present only as activities and not as substances, the unit in which the concentration or the quantity of an enzyme is expressed should be such as corresponds to unit catalytic action. Assuming the reaction not to be markedly reversible, the velocity may be represented by the equation:

$$\frac{dC}{dt} = -HC_1^{n_1}C_2^{n_2}\ldots\ldots, \qquad (1)$$

where C_1, C_2, etc., represents the concentrations of the reacting substances, n_1, n_2, etc., molecular coefficients, t time and H the catalytic activity of the enzyme. Here it is assumed that the reaction is infinitely slow in the absence of the enzyme. In the great majority of well-studied cases H has been found to be proportional to the concentration of the enzyme.
Or

$$H = kE, \qquad (2)$$

where k is the velocity coefficient and E the concentration of the enzyme. K is a function of experimental conditions, more particularly of temperature and coexisting substances. If T represents temperature, and S_1, S_2, etc., the concentrations of the co-existing substances, then

$$k=\phi(T,\ S_1,\ S_2,\ .....). \qquad (3)$$

The velocity with which the enzyme is destroyed is determined by temperature, the reacting and co-existing substances. Hence—if E_o is the initial concentration of the enzyme,

$$E=\psi(E_o, T, C_1, C_2....., S_1, S_2,.....). \qquad (4)$$

The specific feature of the chemical kinetics of enzymes consists in the study of functions (3) and (4). The influence of the co-existing substances is most varied and full of interest. The effect of various excitants and retarding agents falls under this head, and the difference in the behaviour of the same enzyme from different sources will doubtless be traced to such influences. But our present knowledge is too meagre to venture any generalization on this point. We shall therefore treat here only such cases, in which the effect of S_1, S_2, etc., is negligibly small or remains unchanged throughout. Then equations (3) and (4) reduce to

$$k=\phi\ (T) \qquad (5)$$

$$E=\psi(E_o,\ T,\ C_1,\ C_2,\ .....,\ t) \qquad (6)$$

Equation (5) must have the same form as in ordinary chemical kinetics. As the temperature range, over which an enzymatic action can be studied, is necessarily very limited, the effect of temperature upon k can be equally well represented by either of the following equations:

$$k=e^{a(\delta-\delta')}, \qquad (7)$$

or

$$k=e^{\alpha\left(\frac{1}{\tau}-\frac{1}{T}\right)}, \qquad (8)$$

where δ is the temperature in degrees centigrade, δ' the standard temperature at which $k=1$; τ is the same temperature in the absolute scale, and a and α are constants. At the standard temperature equation (2) reduces to

$$H=E.$$

It is usually supposed, in analogy to inorganic catalysers, that a definite quantity of an enzyme can transform an infinite amount of the substratum. This can only be the case where temperature is kept so low, that the velocity of decay of the enzyme through the effect of heat is immeasurably small. But even then it is doubtful whether this can be strictly true. At any rate, the weakening of the enzyme in the course of the reaction is a fact of tolerably general observation. The rate of decay of the enzyme may stand in a very complicated relation to that of the main reaction, but the most probable assumption is that they are proportional to each other. In other words, the destruction of the enzyme takes place in accordance to its catalytic activity, or mathematically expressed:

$$\frac{dE}{dt} = r\frac{dC}{dt}. \qquad (9)$$

In order to form a clear mental image of the mechanism of the catalytic activity of the enzyme as well as that of its decay, let us take the particular case of the decomposition of hydrogen peroxide through the agency of catalase. The velocity of the reaction must be proportional to the number of molecules of hydrogen peroxide, which are in contact with the particles of the enzyme. At every moment this must be proportional to the product of the concentrations of the enzyme and the peroxide. Hence,

$$\frac{dC}{dt} = -kEC. \qquad (10)$$

This is the equation which Senter has demonstrated to hold in the case of blood catalase, when the temperature is low and the concentration of hydrogen peroxide is very small. Indeed, the velocity of a large number of enzymatic reactions is represented by equation (10).

If the enzyme is destroyed by an interaction with hydrogen peroxide, the velocity of destruction must also be proportional to the number of molecules of the peroxide which are in contact with the particles of the enzyme. Hence we may write:

$$\frac{dE}{dt} = -k'EC, \qquad (11)$$

where k′ is the velocity coefficient of the decay of the enzyme. Whatever the nature of the interaction between the enzyme and the substratum may be, it is quite indifferent to the establishment of equation (11). But it is quite probable that catalase is destroyed by oxidation, because other oxidizing agents have also very injurious effect upon it.

From (10) and (11) we have

$$\frac{dE}{dt}=\frac{k'}{k}\,\frac{dC}{dt}, \qquad (12)$$

which is in agreement with (9). From the foregoing it is clear that this equation must hold also in great many cases, where the enzyme is acted upon by the substratum.

Integrating equation (12) we get the relation:

$$E=\frac{k'}{k}\Big(A+C\Big), \qquad (13)$$

where

$$A=\frac{k}{k'}E_0-C_0, \qquad (14)$$

C_0 being the initial concentration of the substratum. It is important to remember that the value of A becomes positive, negative or zero according as kE_0 is greater or less than $k'C_0$ or is equal to it. Equation (13) is a particular case of equation (4) or (6).

Putting this value of E in (10), we have

$$\frac{dC}{dt}=-k'(A+C)C, \qquad (15)$$

from which we see that the reaction may be formally considered to be one of the second order, in which the initial concentrations of the reacting substances differ by the amount A, and the velocity coefficient of which is k′. Equation (15) gives on integration:

$$\ln\frac{C_0}{C}-\ln\frac{C_0+A}{C+A}=k'At, \qquad (16)$$

or

$$C=\frac{k'AC_0}{\substack{k'At\\ kE_0l \qquad -k'C_0}} \qquad (17)$$

If A is positive, the denominator of the right side of equation (17) grows continuously larger with increasing t, so that C must gradually approach zero. In other words, the reaction proceeds to completion with time. This will be the case if the initial concentration of the enzyme is relatively large in comparison to that of the substratum.

On the contrary, if A is negative, the first term of the denominator tends to nil with ever-increasing time, so that C will gradually approach the value

$$C_{\infty} = -A.$$

That is, the reaction will never proceed beyond this limit, because the enzyme will be gradually annihilated. This will be the case when the initial concentration of the enzyme is relatively small in comparison to that of the substratum.

If $A=0$, equation (16) or (17) becomes indeterminate, but then equation (15) becomes formally indentical to that of a reaction of the second order, in which both reacting substances are in equivalent quantities. The integration gives:

$$\frac{1}{C} - \frac{1}{C_o} = k't,$$

or

$$C = \frac{C_o}{1 + k'C_o t} \cdot \qquad (18)$$

Equations (10) and (11) are exactly of the same form, and E can be exchanged for C, if k′ is exchanged for k. Hence we can at once write down the equations which, corresponding to (17) and (18) describe the change of E with time. These equations are:

$$E = \frac{kA' E_o}{k'C_o l^{kA't} - kE_o}, \qquad (17')$$

where

$$A' = \frac{k'}{k} C_o - E_o,$$

and

$$E = \frac{E_o}{1 + k E_o t} \cdot \qquad (18')$$

A′ has the sign opposite to that of A. Hence in the case where the main reaction proceeds to the end, some of the enzyme remain still active even after a very long time. The limiting value is:

$$E_\infty = -A'$$

If A=0, both the substratum and the enzyme tend towards nil with increasing t.

In order to estimate the effect of temperature on the course of the reaction, we must know its influence upon k′. This can also be expressed by an equation similar to (8):

$$k' = e^{\beta\left(\frac{1}{\pi}-\frac{1}{T}\right)}, \qquad (19)$$

where π is the temperature at which k′ becomes equal to unity. The coefficient β will be generally greater than α, so that the ratio $\frac{k}{k'}$ will decrease with rising temperature. Hence, according to equation (12), the velocity of decay of the enzyme must increase more rapidly than the velocity of the main reaction, on elevation of the temperature. The effect of this displacement upon the course of the reaction is perfectly clear because it is equivalent to a greater increase of C_0 in comparison to that of E_0. At a higher temperature the initial velocity will be greater, but it will decrease more rapidly. In the case where the reaction approximates to that of the first order at a lower temperature, it will deviate more and more from the type as the temperature rises. This is what Senter found in the case of catalase obtained from blood.

Putting in equation (18) the values of k and k′ given in (8) and (19), we have:

$$C = \frac{e^{\beta\left(\frac{1}{\pi}-\frac{1}{T}\right)}\left(E_0 l^{\frac{\beta-\alpha}{T}+\frac{\alpha}{\tau}-\frac{\beta}{\pi}} - C_0\right)C_0}{e^{\alpha\left(\frac{1}{\tau}-\frac{1}{T}\right) e^{\beta\left(\frac{1}{\pi}-\frac{1}{T}\right)}\left(E_0 e^{\frac{\beta-\alpha}{T}+\frac{\alpha}{\tau}-\frac{\beta}{\pi}} - C_0\right)t} E_0 e - e^{\beta\left(\frac{1}{\pi}-\frac{1}{T}\right)} C_0} \qquad (20)$$

This is the equation which represents the course of the reaction at different temperatures and under varying initial conditions.

There are four constants in this equation: β, α, π and τ. Of these the last is the standard temperature defined in an appropriate manner. The other three must be evaluated experimentally, and this may be accomplished in the following manner.

Let C_1 and C_2 be the values of C at t_1 and t_2, the latter being so chosen that $t_2=2t_1$. Then, from equation (16) we get:

$$C_2C_o(C_1+A)^2=C_1^2(C_2+A)(C_o+A).$$

Solving this equation for A, we have:

$$A=\frac{2C_oC_1C_2-C_1^2(C_o+C_2)}{C_1^2-C_oC_2},$$

or

$$A=0.$$

Putting the former value of A in (16) we can calculate k′ from the experimental data. From the values of k′ at different temperatures β and π can be evaluated. Equation (14) then enables us to find the values of k at different temperatures, and from these α can be deduced.

Mr. E. Yamasaki has studied with utmost care the course of decomposition of hydrogen peroxide by catalase obtained from young shoots of bamboos, Phyllotachys mitis, Riv. His results confirm the foregoing deductions in a most remarkable manner, and equation (20), in a somewhat modified form, has been found quite adequate to represent a tolerably large mass of experimental data. His method of evaluating the constants differs somewhat from the one given above and is perhaps better suited for the purpose.

Let us now turn our attention to the case, in which the effect of the substratum and the product of its transformation as well as the effect of the co-existing substances upon the rate of decay of the enzyme remain practically constant through the whole course of the reaction, and consider the interesting problem of the so-called optimum temperature. Equation (4) takes now the simple form:

$$E=\psi(T, t)$$

This relation has often been the subject of study and the equation

$$E=E_0e^{-e^{\beta\left(\frac{1}{\pi}-\frac{1}{T}\right)t}} \qquad (21)$$

has been found to hold in a great many cases. The experiments were indeed mostly performed in the absence of the substrata. It is probable that the presence of the latter would modify the value of β, because many substrata are known to exercise a protective action upon the enzymes; but the form of the equation will not be modified thereby.

When the reaction is one of the first order with respect to the concentration of the substratum, then the velocity is represented by the equation:

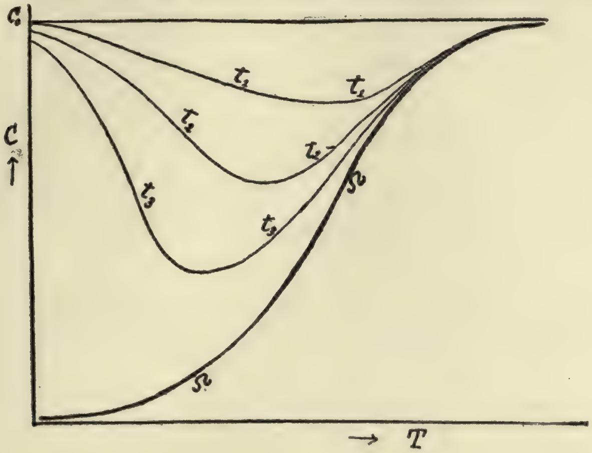
$$\frac{dC}{dt}=-E_0e^{\alpha\left(\frac{1}{\tau}-\frac{1}{T}\right)}e^{-e^{\beta\left(\frac{1}{\pi}-\frac{1}{T}\right)}t}C\,,$$

which, on integration, gives:

$$\ln\frac{C_o}{C}=-E_0e^{\alpha\left(\frac{1}{\tau}-\frac{1}{T}\right)-\beta\left(\frac{1}{\pi}-\frac{1}{T}\right)}\left(1-e^{-e^{\beta(\frac{1}{\pi}-\frac{1}{T}}t}\right) \qquad (22)$$

This is essentially the equation first given by *Tammann.*

As it has been repeatedly pointed out, the notion of the optimum temperature has a definite meaning only when the time interval is fixed, during which the enzymatic action takes place. A graphical representation of equation (22), in which definite values are assigned to t, will make the meaning of the optimum temperature quite clear. In the equation there are three variables, C, T and t. But, when the value of the last is fixed, we have a relation between C and T, which can be represented by a curve. In the annexed diagram the curves for different values of t are shown. Ω Ω is the curve for $t=\infty$. This curve represents



the fact that at a high temperature the enzyme is destroyed so rapidly that the reaction proceeds only a little way and then stops. At a lower temperature the reaction proceeds further before the enzyme is completely annihilated. This is evidently the limiting curve and the curves for limited duration must all lie above it, and indeed the higher as the time allowed is the shorter. The minimum points of the curves represent the temperatures at which the reaction proceeds the furthest in the given intervals. From the figure, we see that the optimum temperature is the higher as the duration of the reaction is the shorter. This relation can be more precisely deduced in the following manner.

Differentiating equation (22) with respect to T, t being assumed to remain constant, we get:

$$\frac{1}{E_0}\,\frac{d\ln C}{dT} =$$

$$e^{\frac{\alpha}{\tau}-\frac{\beta}{\pi}\frac{\alpha-\beta}{T}}\left\{\left(\frac{\alpha-\beta}{T^2}+\frac{\beta}{T^2}e^{\beta\left(\frac{1}{\pi}-\frac{1}{T}\right)}t\right)e^{-e^{\left(\beta\frac{1}{\pi}-\frac{1}{T}\right)t}}+\frac{\alpha-\beta}{T^2}\right\}$$

For the optimum temperature the right side of this equation must vanish. Hence,

$$\left(\alpha-\beta+\beta e^{\beta\left(\frac{1}{\pi}-\frac{1}{T}\right)}t\right) e^{-e^{\beta\left(\frac{1}{\pi}-\frac{1}{T}\right)}t}+\alpha-\beta=0.$$

On taking the logarithm and transforming, we get

$$\left(e^{-\frac{\beta}{T}}t\right)=e^{-\frac{\beta}{\pi}}\ln\frac{\beta e^{\frac{\beta}{\pi}}\left(e^{-\frac{\beta}{T}}t\right)+\alpha-\beta}{\beta-\alpha}$$

Now it is clear that this equation will be satisfied by a definite value of the term in brackets. Let this value be e^h, then

$$e^{-\frac{\beta}{T}}t=e^h,$$

or

$$\frac{\beta}{T}=\ln t-h. \qquad (23)$$

In order to eliminate h, let Θ be the optimum temperature for $t=1$. Then from the foregoing equation,

$$T=\frac{\beta}{\Theta\ln t+\beta}\Theta$$

and

$$\Theta=\frac{\beta}{\beta-T\ln t}T.$$

If Θ is determined under constant conditions well defined with respect to the coexistent substances, etc., it may be regarded as one of the characteristics of the enzyme. But for the purpose of characterization β is evidently more suitable than Θ. If T_1 and T_2 are the optimum temperatures for the durations t_1 and t_2 respectively, then we get from (23)

$$\beta=\frac{\ln t_1-\ln t_2}{\frac{1}{T_1}-\frac{1}{T_2}}.$$

In this way the value of β can be determined in presence of the substratum, and this is most probably of greater practical significance than the value of β measured in its absence, as it is usually the case.

The problem of the maximum temperature is completely covered by equation (22) as far as the decay of the enzyme can be considered as a reaction of the first order, and does not present any feature of theoretical interest.

SUMMARY

Some problems regarding the decay of the enzyme in the presence of the substratum have been investigated. The particular case, in which the velocity of destruction of the enzyme is proportional to that of the transformation of the substratum, has been discussed in detail and several interesting consequences have been deduced. These have received full confirmation from the experimental studies on catalase by Yamasaki. Then the problem of the optimum temperature has been treated, and the relation between this temperature and the temperature coefficient of the decay of the enzyme has been elucidated.

Abstract

CAOUTCHOUK-BENZENE (C_6H_6)—WATER

By W. P. A. Jonker
Goes, Holland

The benzene solution of caoutchouk gives a partial dismixing with water. The system is reversible, therefore the phase rule can be applied. Three liquid layers are formed, of which the concentration was fixed at 30° C.

THE MELTING POINTS OF FIRE BRICKS

By C. W. Kanolt
Bureau of Standards, Washington, D. C.

We are accustomed to thinking of a melting point as a temperature at which a substance changes from a condition in which it does not flow perceptibly under its own weight to a condition in which it flows readily. However, no rational definition of the melting point can be based upon this conception. For example, when glass is heated, the transition from its ordinary condition to a distinctly fluid condition is a very gradual one and occupies a range of several hundred degrees. Some other substances which possess perfectly definite temperatures of transition to a fluid phase, undergo changes resembling fusion at lower temperatures. Solids in general become softer when heated; they may become so soft as to yield to their own surface tension, with the result that sharp corners are rounded off. Rutile, in its natural, slightly impure condition, melts at about 1700° C. The melting point is very definite, there being a sharp transition from a rather soft solid to a liquid of low viscosity, with a considerable absorption of heat. Yet at temperatures 100 degrees or more below the melting point, corners are rounded off and small particles become sintered together. The sintering of clay is probably a similar phenomenon of surface tension. Clay exists generally in the form of extremely fine particles, its unusually slight solubility in water accounting for this condition. Fine particles are more readily united by surface tension than large ones.

A melting point can be precisely and rationally defined only as the temperature at which a crystalline or amisotropic phase and an amorphous or isotropic phase of the same composition can exist in contact in equilibrium. In harmony with this, one might define a solid as a crystalline substance, and a fluid as a substance not crystalline; however, these definitions of solid and fluid would lead to results quite different from our ordinary conceptions, as they would require us to consider glass, even silica glass, as a fluid, and certain "anisotropic liquids" whose viscosities are even less than that of water, as solids. Perhaps it is better to leave solid and liquid or fluid as general terms without precise definitions.

While the above definition of melting point is satisfactory for the case of a pure substance, so complex a mixture as an ordinary fire brick usually has no single definite melting point according to this definition, since several anisotropic phases may be present, all differing in composition from the isotropic phase produced by fusion. We can then only select the temperature at which the transition from a rigid to a fluid state seems most distinct, and can call this the melting point only by apology.

In the case of fire bricks, the transition temperatures so found are fortunately sufficiently definite to make their determination of practical value. I have taken as the melting point the lowest temperature at which a small piece of the brick could be distinctly seen to flow. Experiments showing the degree of definiteness of this temperature will be described.

The melting point of a brick is, of course, not the only property to be considered in determining its fitness for a given purpose. Its crushing strength cold, its behavior under load conditions when heated, and its resistance to fluxes may all be important. The present paper deals only with melting points.

A large number of the brick samples tested were kindly furnished by Dr. A. V. Bleininger, being identical with samples tested by Bleininger and Brown[1] under load conditions at 1300° C., this work being carried out at the Pittsburgh Testing Station of this bureau, which station was at that time the Technologic Branch of the United States Geological Survey. The chemical composition, crushing strength cold, porosity and density of these samples are given by Bleininger and Brown. They also determined the Seger cone numbers corresponding to the softening temperatures of the bricks.[2]

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[1] Bureau of Standards Technologic Paper No. 7 (1912).

[2] See also: Hofman and Demond, Trans. Am. Inst. Mining Eng. *24*, p. 42 (1894); Hofman, Trans. Am. Inst. Mining Eng., *25*, p. 3 (1895), *28*, p. 435 (1898); Hofman and Stroughton, Trans. Am. Inst. Mining Eng., *28*, p. 440 (1898); Gary, Mitt. k. tech. Versuchsanstalten *14*, p. 63 (1896); Jochum, Thonindustrie Zeit., *27*, p. 764 (1903); Weber, Trans. Am. Inst. Mining Eng. *35*, p. 637 (1904).

It is difficult to interpret results obtained with Seger cones in terms of actual temperatures, for it has been shown by Simonis[1] that the falling over of Seger cones, of certain numbers at least, depends not only upon the temperature, but also to a large extent upon the rate of heating. This observation has been confirmed in this laboratory, using the cone numbers having softening temperatures in the same range as fire brick, and it has appeared that in many cases the melting point of a fire brick, defined as stated above, is more definite than the softening temperature of the corresponding Seger cone. It has, therefore, appeared preferable to use a more direct and more accurate method of determining temperatures.

The experiments were conducted in an Arsem graphite resistance vacuum furnace[2] (Fig. 1). In some preliminary experiments upon fire bricks, samples were heated in graphite crucibles, and exposed to such gases as might remain in the furnace. Although the pressure was kept as low as two millimeters of mercury, there was still a slight reducing action upon the brick, and some samples were blackened superficially. Subsequent work has shown that the action was insufficient to produce any very great difference in the results, but, as a matter of precaution, the specimens were protected by a refractory tube (A, Fig. 1) being placed upon a bed of white alundum (fused alumina) in the bottom of the tube. This tube was supported by the brass collar, B, in which it was made to fit tightly by winding with asbestos string, or otherwise, and which was soldered to the lead gasket by which the joint C in the top of the furnace was made air tight.

The refractory tubes were made of a mixture of 72% kaolin and 28% alumina, these being the proportions for the formation of sillimanite, Al_2O_3,SiO_2. According to Shepherd and Rankin[3] pure sillimanite melts at 1811°. The sillimanite tubes were found to melt at about this temperature. Kaolin tubes were used for some samples of relatively low melting points. Either sillimanite or kaolin tubes were used with all fire bricks melting below 1800°. The chromite and magnesia bricks were melted in graphite crucibles without protecting tubes. The experiments were made rapidly and the graphite had little action on the samples until after fusion had occurred and the melting point had been determined. Magnesia tubes may be used in place of sillimanite tubes, and they have the advantage of a higher melting point, but all magnesia tubes that have been tried have been found to be very easily cracked by changes of temperature, and to be so porous as to afford little protection from the gases of the furnace. When a sillimanite or kaolin tube was used, twenty to thirty minutes was consumed in heating the furnace to a little below the melting point of the sample. This initial heating could be preformed much more quickly, so far as the furnace is concerned, but more rapid heating would be likely to crack the tube. When the temperature had nearly reached the melting point it was raised much more slowly. When these protecting tubes were used, the samples showed only very slight signs of reduction. In certain experiments made with this apparatus, for example the determination of the melting point of platinum as a check upon the work, it has been desirable to still further diminish the chances of the presence of reducing gases. This has been accomplished by the device shown at D in Fig. 1, which consists of a glass tube drawn out into a fine capillary and leading into the furnace. An outer brass tube protects the capillary. This capillary admits a slow current of air to the inside of the refractory tube, and the air passes out through the pores of the tube into the interior of the furnace. By working the vacuum pump continually the pressure in the furnace was kept down to a few millimeters of mercury, in spite of the influx of air. This process was, of course, injurious to the graphite heater, but several such experiments could be made with one heater before it was burned out.

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[1] Simonis, Tonisdustrie Zeit. *32*, p. 1764 (1908).

[2] Arsem, Jour. Am. Chem. Soc., *28*, p. 921 (1906); Trans. Am. Electroch. Soc., *9*, p. 153 (1906).

[3] Shepherd and Rankin, Am. Jour. Sci., *28*, p. 301 (1909).

While the sample was being heated it was observed through the window E at the top of the furnace. A glass window was used here in place of the mica window provided by the makers of the furnace. The glass was attached by a mixture of rosin and beeswax. To keep this material cool an additional water jacket, F, was applied to the part of the furnace projecting above the water of the tank.

The temperatures were determined by means of a Morse optical pyrometer of the Holborn-Kurlbaum type,[1] which was sighted vertically downward through the furnace window. The current in the pyrometer lamp was measured with a Siemens and Halske milliammeter with a shunt. This instrument was calibrated several times, and its very small temperature coefficient was taken into account. Its readings are certainly reliable to .001 ampere and probably to .0005 ampere.

The carbon-filament pyrometer lamp was one of the standard lamps of the bureau, and had been thoroughly aged, and had been accurately calibrated by several observers before the beginning of the investigation, and again, by a different method, toward its close. In the first calibration it was sighted into a platinum resistance furnace in which black body conditions were obtained, and the temperature of which was measured by platinum, platinum-rhodium thermocouples. These thermocouples had been calibrated against the freezing points of pure metals. In the second calibration the lamp was calibrated against the freezing points of metals directly, without the intermediation of thermocouples. The metals used were copper, silver, and the copper-silver eutectic, which freeze at 1083°, 961°, and 779° respectively. These were placed in Acheson graphite crucibles of the form shown in Fig. 2, about 100 grams of metal being used in each. The pyrometer was sighted downward into the central graphite tube, of which the inside diameter was 6 mm and the wall thickness 1 mm. The crucibles were heated or cooled gradually, while observations were made every ten to twenty seconds, and the resulting heating or cooling curves were plotted. A typical curve is shown in Fig. 3. In this diagram, a change of temperature of 1° corresponds to a change of current of about .0005 ampere. By means of the three known temperatures, the relation between the current in the lamp and the temperature was expressed in the form, $C = a + bt + ct^2$.

This method presented two possible sources of error to be especially considered, namely, the conduction of heat along the inner graphite tube, and the departure of the interior of this tube from black-body conditions. If the conduction of heat along the tube introduced appreciable error, the observed temperatures would be too high with rising temperature, when the furnace heater would be hotter than the metal, and too low with falling temperature, when the reverse would be true. The fact that the results from the heating curves obtained with copper and silver were in very close agreement with those from the cooling curves shows that the errors from conduction are negligible; and these and numerous other observations have indicated that such a tube when made of graphite, which is itself nearly perfectly black, is a very good black body. Using the copper-silver eutectic somewhat unsatisfactory results were obtained with heating curves, the trouble appearing to be in the behavior of the alloy rather than in the temperature measurement. In this case only cooling curves were used for the calibration. The calibration of the lamp at this temperature is relatively unimportant, since none of the melting points here given correspond to a lamp temperature below the melting point of silver. The results of this calibration agreed with those obtained by the first method within one degree from 700° to 1300°, which includes all lamp temperatures used in this work. Near the close of the investigation the pyrometer lamp was accidentally overheated, and it was necessary to recalibrate it. This time, only the cooling curve method was used.

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[1] Holborn and Kurlbaum, Sitzber. d. k. Akad. d. Wissensch. zu Berlin, June 13, p. 712 (1901); Ann. der Phys., *10*, p. 225 (1902); Waidner and Burgess, Bull. Bureau of Standards, *1*, No. 2 (1904); Mendenhall, Phys. Rev., *33*, p. 74 (1911); Henning, Zeit. f. Instrumentenkunde *30*, p. 61 (1910).

As the melting points to be measured were above the working limit of the pyrometer lamp, an absorption glass was interposed between the pyrometer and the furnace. This glass was calibrated as follows. In the Arsem furnace was placed a graphite crucible, the interior of which, when the furnace was hot, furnished a field of very uniform brightness. A steady current was passed through the furnace and the temperature allowed to become stationary. The temperature was then measured with the pyrometer, and also the apparent temperature as observed through the absorption glass. If T_1 is the absolute temperature, observed without the glass, and T_2 is the apparent absolute temperature observed with the glass, we have the following relation, which is easily deduced from the Wien radiation law,

$$\frac{1}{T_2} - \frac{1}{T_1} = A$$

The constant, A, was determined in this way with several different furnace temperatures, and the results were in close agreement. The mean value of A was .0002249. The values of the constants of Wien's law do not enter into the work.

The glass furnace window absorbed and reflected a small amount of light and it was necessary to apply a correction for this. The constant of this glass was determined in the same way as that of the absorption glass, and was found to be .0000040. The correction in degrees depends of course upon the temperature; it is about 15° at the melting point of ordinary fire brick.

As a check upon the whole apparatus, a determination of the melting point of platinum was made. A piece of platinum foil was placed within two magnesia tubes, one within the other, in the place of the single tube shown at A (Fig. 1), and a slow current of air was admitted at D. Fairly good black body conditions were obtained but the platinum was faintly visible. The observed melting point was 1750°. The value accepted by the Bureau of Standards as the melting point of platinum is 1755°. After the pyrometer lamp had been overheated and recalibrated, this test was repeated. In place of magnesia tubes, tubes of a mixture of magnesia and alumina,[1] obtained from the Königliche Porzellan-Manufactur, Berlin, were used. These were found to be more satisfactory than magnesia tubes, being much less porous and less easily cracked. The material softens at a little above the platinum point. Using a single tube the value 1746° was obtained, with two tubes 1750°. Tests were also made in an iridium tube furnace where there was no possibility of a reducing atmosphere. So good black body conditions were obtained that the platinum was quite invisible. A piece heated to 1747° and removed was found not melted; one heated to 1759° and removed was found melted.

The use of the optical pyrometer depends upon the assumption that the object sighted upon emits black-body radiation. This is the case if the object is within a vessel at uniform temperature, and is viewed through a relatively small opening in the vessel.

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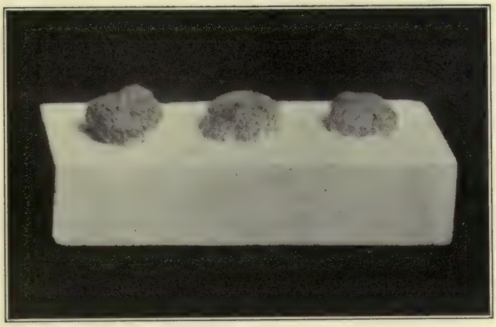
[1] Heinecke, Zeit. angew. Ch., *21*, p. 687 (1908).

This can readily be accomplished in the apparatus used, but under such conditions it would be impossible to distinguish the sample, owing to the uniform brightness of the sample and its environs. In practice, the sample was placed slightly below the hottest part of the furnace, in such a position as to be barely distinguishable. This requires only a temperature difference of about five degrees. When the temperature of a sample had almost reached the melting point, the temperature was raised more slowly and the sample was observed continually. When it was seen to melt, a final temperature measurement was made and the heating current was immediately stopped, thus preventing the temperature from rising any higher. The observation was then verified by an examination of the sample after its removal from the furnace.

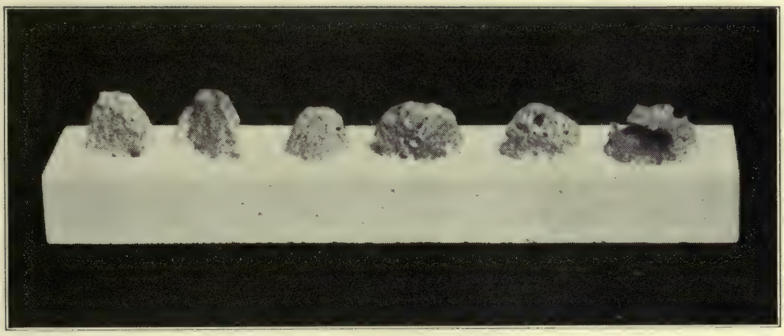
An idea of the degree of definiteness of the melting points may be obtained from Fig. 4 and Fig. 5, in which are shown samples which have been heated to successively higher temperatures. Fig. 4 may be taken to represent the usual degree of definiteness. The sample heated to 1680°C. appears unaffected; that heated to 1695° shows very slight signs of fusion; that heated to 1705° is completely fused. 1705° was taken as the melting point. Fig. 5 shows perhaps the least definite melting point found. Complete fusion occurred at 1620°, but there was partial fusion at considerably lower temperatures, 1600° was taken as the melting point.

Near the melting point, samples were heated at the rate of about ten degrees per minute. This rate of heating was quite slow enough, as a temperature measurement can be made in a few seconds and a slower rate of heating near the melting point was found to give the same results. The entire time required for heating a sample from room temperature to its melting point was thirty to forty minutes. Experiments were made to determine whether samples could undergo any change in melting point as the result of heating in the vacuum furnace. Samples of various kinds were heated in the furnace to about 1550° for about six hours, and their melting points were then determined. The results are given in Table I.



1680° 1695° 1705°

FIGURE 4



1570° 1580° 1590° 1600° 1610° 1620°

FIGURE 5

TABLE I

Sample Number	Material	Determinations of melting point without previous heating	Determinations of melting point after six hours heating
14	Fire clay	1635°	1655°
		1630°	1655°
27	Fire clay	1600°	1635°
		1610	1630
		1600	1635
		1585	1640
		1595	
48	Fire clay	1710°	1705°
		1705	1695
		1705	
		1700	
		1705	
20	Bauxite	1740°	1740°
		1745	1730
41	Silica	1705°	1695°
		1700	1700
		1695	
		1695	

It appears from the table that Nos. 14 and 27, which are bricks of low melting point, melted at a somewhat higher temperature after long heating; while the other bricks were unaffected. The melting point of No. 27 is less definite than that of most bricks. This increase of melting point might be accounted for upon the assumption that the brick consisted of two materials existing in distinct particles, one sort having a lower melting point than the other, these two materials becoming run together after long heating near the melting point, producing a material of higher melting point than that of the more fusible of the original materials. The appearance of samples of No. 14 and No. 27 after heating for a short time to near the melting point supports this explanation. Sample No. 27 is shown in Fig. 5. After the six hours heating they appeared more uniform. Long heating in a vacuum would tend to vaporize the more volatile constituents of the brick, and this might produce an appreciable increase of melting point.

The most common fire brick are those made of clay, of which the essential ingredient is kaolin, $Al_2O_3,2SiO_2,2H_2O$. Shepherd and Rankin[1] found that the only compound of alumina and silica that can exist in the neighborhood of the melting points is sillimanite, Al_2O_3,SiO_2. It follows that clay when near its melting point is no longer a single compound but a mixture of Al_2O_3,SiO_2 and SiO_2. Hence the melting point of pure kaolin, like that of fire brick, can not be expected upon theoretical grounds to be perfectly definite, but fairly definite results are obtained when the visible flow is taken as the criterion of fusion, as in the case of fire brick. Two samples of white kaolin, one English, the other probably English also, both melted at 1740°. A sample of brownish white German kaolin melted at 1735°. Therefore the highest melting point that can be attained in brick containing nothing more refractory than kaolin is 1740°. When an excess of alumina is present, as in bauxite brick, the melting point may be higher.

A few brands of silica brick were tested. Pure silica melts at about 1600°.[2] However, the fused silica possesses such extreme viscosity near the melting point that it does not flow or change shape distinctly until considerably higher temperatures are reached. I have obtained 1750° as the *apparent* melting point of pure silica, *i.e.*, the temperature at which it flows distinctly. This temperature, however, is naturally a very indefinite one. The temperature at which silica bricks flow distinctly is more definite.

Bauxite brick are made from bauxite, $Al_2O(OH)_4$ containing usually considerable quantities of other material. Bauxite, of course, becomes converted to alumina, Al_2O_3, when heated. Pure alumina melts at about 2010°.[3] None of the bauxite bricks examined approached this melting point. A single sample of bauxite was tested and found to melt completely at 1820°, the center of the nodules melting at 1790°. A sample of bauxite clay melted at 1795°.

One brand of magnesia brick was examined and found to melt at 2165°. The melting point of pure magnesia is more or less in doubt at present. It is certainly much higher than that of the impure magnesia brick. This brick contained a large quantity of iron and was of a dark brown color. When heated for a few minutes to near its melting point it became white. This occurred both in the electric vacuum furnace and in an oxy-hydrogen flame. It might result either from the vaporization of the iron, or from the formation of a colorless compound of iron and magnesia. An analysis of the specimens has shown that the heated samples contain much less iron.

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[1] Loc. cit.

[2] Day and Shepherd, *Jour. Am. Chem. Soc.*, *28*, p. 1089 (1906).

[3] A paper on the melting points of pure refractory oxides is in preparation.

One brand of brick made from chromite, FeO,Cr_2O_3, was examined. It was found to melt at 2050°. A sample of natural chromite from a different source melted at 2180°.

Silicon carbide, SiC, has been used as a refractory material. At very high temperatures it decomposes without melting. Tucker and Lampen[1] state that it decomposes at 2220°. Results in close agreement with this have been obtained by Gillett[2] and by Saunders.[3] This is undoubtedly correct for decomposition under ordinary conditions, but silicon carbide can be heated for a short time to much higher temperatures without complete decomposition. It was thought that by very rapid heating it might be possible to reach the melting point of the silicon carbide before decomposition was complete, although such a melting point would probably have only theoretical interest. With this object, a few grams of silicon carbide was placed in a graphite crucible, which was placed in a second larger graphite crucible to give more uniform temperature and the whole was heated in an arc furnace at atmospheric pressure, the temperature being measured by sighting the optical pyrometer through a narrow graphite tube inserted in the top of the crucible. A temperature of 2700° or more was reached and was maintained for a few minutes. The silicon carbide was about half decomposed, leaving a residue of carbon, but showed no indication of fusion.

The results for fire brick will be found in Table II. Samples 1 to 26 are identical with the samples of the same numbers studied by Bleininger and Brown.[4] All the bricks tested were made in the United States. Each melting point given is the mean of at

[1] Tucker and Lampen, *Jour. Am. Chem. Soc.*, *28*, p. 853 (1906).
[2] Gillett, Jour. Phys. Chem., *15*, p. 213 (1911).
[3] Paper presented before the American Electrochemical Society, May, 1912.
[4] Loc. cit.

least two determinations. The mean of the melting points of the 41 samples of fire clay bricks is 1649°.

TABLE II

FIRE CLAY BRICK

Sample Number	Melting Point	Sample Number	Melting Point
1	1630	26	1695
2	1635	27	1600
3	1605	28	1695
4	1605	29	1595
5	1705	30	1560
6	1705	31	1600
7	1700	32	1650
8	1700	33	1655
9	1675	34	1570
10	1710	35	1650
11	1660	36	1590
12	1555	37	1650
13	1635	38	1660
14	1630	47	1725
15	1655	48	1705
17	1650	49	1715
21	1615	53[1]	1635
22	1640	54[1]	1635
23	1660	55[1]	1685
24	1660	56[1]	1605
25	1715		

BAUXITE BRICK

Sample Number	Melting point
19	1760
20	1740
44	1720
45	1785
46	1720
50	1665
51	1565
52	1590

[1] Samples 53, 54, 55 and 56 are of the same brands as 4, 9, 7 and 17 respectively, but from different lots.

SILICA BRICK

Sample Number	Melting point
39	1700
40	1705
41	1700

CHROMITE BRICK

Sample Number	Melting point
42	2050

MAGNESIA BRICK

Sample Number	Melting point
43	2165

The analyses of a large number of the fire clay bricks studied are available,[1] but it does not seem possible to establish any very definite relation between composition and melting point. Since the bricks contain about eight different constituents in quantities sufficient to affect the melting point, and since the melting point may also be affected by lack of homogeneity in the material, it is obvious that a prediction of the melting point upon the basis of a chemical analysis would be uncertain. If the melting points are compared with the results of tests under load conditions at 1300°,[2] it is evident that there is little relation between the two.

SUMMARY

1. The melting points of 54 samples of fire brick, including fire clay, bauxite, silica, magnesia, and chromite brick, have been determined in an electric vacuum furnace, the temperature being measured with an optical pyrometer (Table II).

2. The following melting points of materials important in the manufacture of fire brick were determined:

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[1] Bleininger and Brown, loc. cit.

[2] Bleininger and Brown, loc. cit.

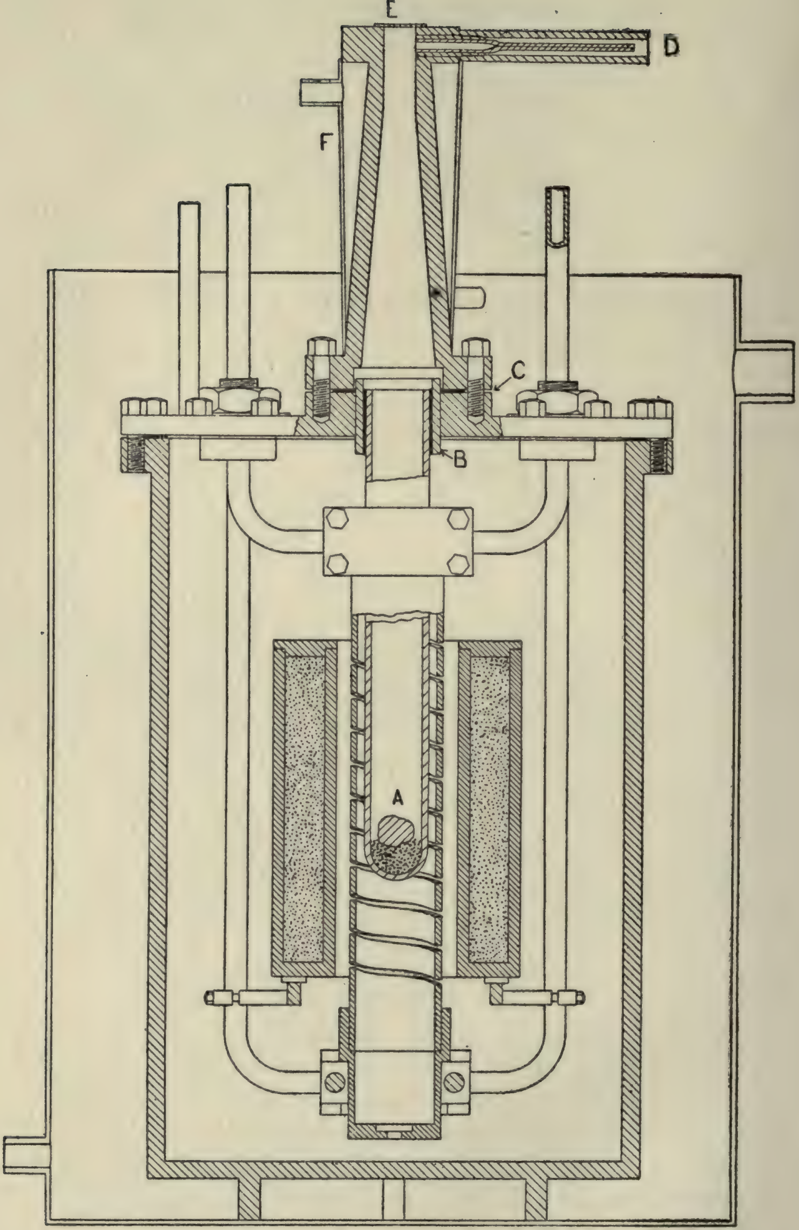

FIGURE 1

Kaolin	1740°
Pure alumina	2010°
Pure silica	1750°[1]
Bauxite	1820°
Bauxite clay	1795°
Chromite	2180°

3. An improved method of calibrating the Holborn-Kurlbaum optical pyrometer is described.

Mr. H. P. Greenwald and Mr. S. E. Moore have rendered efficient assistance in carrying out this work.

[1] This is not the true melting point but represents approximately the temperature at which silica flows distinctly.

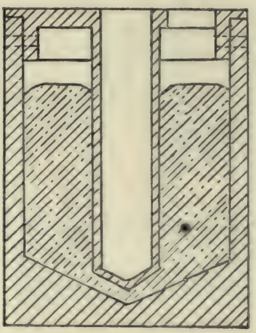

Figure 2.

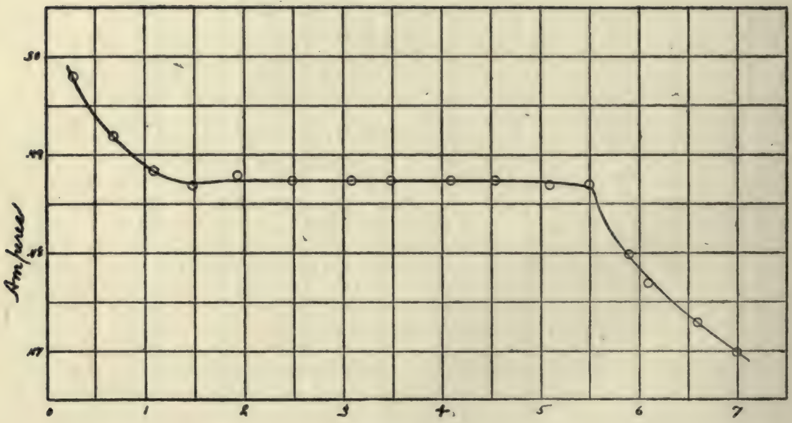

Figure 3.

ON THE PRESENT THEORY OF MAGNETISM AND THE PERIODIC SYSTEM OF CHEMICAL ELEMENTS

By Jakob Kunz

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This paper contains the following topics:

1. Fundamental assumptions.
2. Experimental facts; diamagnetism, additive and non-additive properties.
3. The periodic system of the elements and their magnetic properties.
4. Ferromagnetism.
5. The magneton of Weiss and the degrees of freedom.

I

FUNDAMENTAL ASSUMPTIONS

The electron theory seems to account for the magnetic phenomena in a very direct way. Indeed, we have only to assume that the molecular currents of Ampère, which form the elementary magnets, are revolving electrons, in order to express Ampère's theory of magnetism in terms of the electron theory. A closer study of the electronic orbits, however, due to Voigt and J. J. Thomson, showed that these currents cannot account sufficiently for the phenomena of diamagnetic and paramagnetic bodies. It was only on the basis of the researches of P. Curie, that P. Langevin was able to give a more satisfactory theory of diamagnetism and paramagnetism. Curie found that the diamagnetic susceptibility is independent of the temperature, while the paramagnetic susceptibility is inversely proportional to the absolute temperature. Langevin concluded, therefore, that there is a fundamental difference between diamagnetic and paramagnetic properties. In Langevin's theory the diamagnetism is a characteristic property of each molecule which contains a certain number of revolving electrons. If the resultant magnetic moment of these electrons in an atom is zero, then the body is diamagnetic; the action of an external magnetic field consists in a change of the orbit, the diamagnetic modification of the atom. If the revolving electrons possess a resultant magnetic moment, the body is paramagnetic. Matter in all its forms is diamagnetic; paramagnetism, whenever it appears, covers, as it were, the diamagnetism without transition between the two distinct groups. Langevin insists that the paramagnetic constants are very large in comparison with the diamagnetic constants. Consider an electron of mass m and charge e revolving with velocity v in an orbit of radius r, the plane of which is perpendicular to a magnetic field H, the centifugal force is balanced by an elastic force f. Without a magnetic field we have

$$\frac{\mathrm{mv}^2}{\mathrm{r}} = \mathrm{fr}.$$

If the magnetic field acts on the electron its velocity will not be changed, but the radius of the orbit will suffer a change. Let the new radius be r^1, then:

$$\frac{\mathrm{mv}^2}{\mathrm{r}^1} = \mathrm{fr}^1 - \mathrm{Hev}$$

and the change of the magnetic moment of N electron per unit volume is equal to:

$$\Delta\mathrm{M} = \frac{-\mathrm{He}^2\mathrm{Nr}^2}{2\mathrm{m}} = -k\mathrm{H}$$

The diamagnetic susceptibility k is therefore equal to:

$$k = \frac{\mathrm{N}}{2}\,\frac{\mathrm{e}^2}{\mathrm{m}}\,\mathrm{r}^2$$

If now the magnetic moment of all the revolving electrons in the atom in an external point is zero, then the substance is purely diamagnetic and the diamagnetic susceptibility k independent of the temperature, if the number of revolving electrons N and the radius of the orbits are not affected by the temperature. If the electronic orbits have a resultant magnetic moment in an external point, then these magnets will be directed by the magnetic field and constitute a paramagnetic body, and both the thermodynamic and kinetic treatment of the problem show that the paramagnetic susceptibility is inversely proportional to the absolute temperature. In addition Curie concluded that a change of physical or chemical state has hardly any influence on the diamagnetic properties.

II

EXPERIMENTAL FACTS

The phenomena are far more complicated than this theory of Langevin indicates. The positive paramagnetic values are on the whole not larger than the negative diamagnetic ones, as is shown by the following table: k is the susceptibility per unit volume,

	$k\ 10^6$		$k\ 10^6$
Pb	−1.37	Al	+1.8
Au	−3.07	Be	+0.29
C (Diamond)	−0.49	B	+4.32
C (amorphous)	−2.02	Mg	+0.57
Hg	−2.6	Na	+2.2
Ag	−1.4	Pd	+5.15
Bi	−13.7	Pt	+29.0
Cd	−1.16	Si	+0.2
Tl	−4.6	N	+0.0537
Cu	−0.82	Mo	2.2
		Os	0.62

Certain elements seem to exist in both the diamagnetic and paramagnetic state. Thus, for hydrogen, I find in Boernstein-Landolts tables: the value +0.008, while Dewar[1] gives a negative value, the magnetic properties of elementary gases and vapors are still insufficiently known. This is, for instance, true for nitrogen. Boron, carbon and silicon seem also to exist in the diamagnetic and paramagnetic state. H. E. Dubois and K. Honda[2] give for crystalline silicon +0.12 and amorphous −0.14. In this respect tin seems to have the most interesting properties. If diamagnetic gray tin is slowly heated, at 32°, k $(= -0.29)$ changes almost suddenly and at 35° passes through zero. Possibly this change would wholly take place at the point of transformation 18°, but then at a much slower rate. Further heating continuously increased k so that at about 50° the value +0.03 for paramagnetic tetragonal tin was reached, which afterwards remained practically constant. At 161° nothing particular was noticed. At the melting point a discontinuity from +0.03 to −0.04 once more appeared; the diamagnetic liquid metal remained nearly unchanged.

[1] Rapports du congres international de physique, vol. 2, p. 506 (1900.)
[2] Acad. Weteuschap. Amsterdam Proc. 12, p. 596-602 (1909-10).

The paramagnetic susceptibility is independent of the temperature over an interval of as much as 500° in the following elements: Na, Al, K, V, Cr, Nb, W, Os; the paramagnetic susceptibility increases with increasing temperature for the elements: Ti, V, Cr, Mn, Mo, Ru, Rh, Tr, Th. These are all exceptions from Curie's rule; it seems to me not justified, to maintain this rule, as there are many more exceptions than confirmations. The same is true for the diamagnetism. Here in a few cases the susceptibility increases with increasing temperature, while for the following elements the diamagnetic susceptibility decreases with increasing temperature: C(amorphous), Cu, Zn, Zr, Cd, Jn, Sb, Te, J, Tl, Pb, Bi (0−268). There are only very few elements which do not vary within the whole temperature range. The starting point of Langevin's theory is undermined. If we consider the magnetic properties of the elements in the periodic system, we find a certain periodic change of the diamagnetic and paramagnetic properties. A very striking exception is given by oxygen, which is strongly paramagnetic; but if oxygen combines with the paramagnetic elements Be, Mg, Al, Mo, W, Th, it forms diamagnetic oxides. The oxides of metals in general are very interesting in this respect, for instance, FeO is weakly magnetic, Fe_2O_3 is stronger and Fe_3O_4 is very strongly magnetic. A strongly magnetic oxide is also Cr_5O_9. At all events, the diamagnetism is a largely non-additive property in inorganic compounds; and the magnetic properties depend so much on chemical and physical influences that one might be inclined to ascribe them to electrons, which are revolving on the surface of the atom. In organic compounds, however, it has been shown by P. Pascal that the molecular susceptibility χ_m is an additive property of the atomic susceptibility χ_a, such that

$$\chi_a = \Sigma a \chi_a + \lambda$$

where λ is a correcting term depending on the structure of the compound being= in the saturated compounds, but amounting to over 6% in certain nonsaturated groups. Oxygen plays in these compounds a very interesting role. Bound up with two different atoms, $-CH_3C_2HOH-$ it is diamagnetic, its atomic susceptibility being -48.10^{-7}. Oxygen by two bonds connected with one carbon atom is still diamagnetic, if this carbon atom—$CH_3CO\ OH$—is connected with a second oxygen atom, the atomic susceptibility is

-35.10^{-7}. Oxygen—CH_3COCH_3—with a double bond connected with C, which carried no other O, is paramagnetic, and its magnetic susceptibility is $+18.10^{-7}$. In more complicated compounds, however, the structure has a great influence on χ. For two groups, the halogenes and intriles, exceptions have been found to the rule of additivity.

III

THE PERIODIC SYSTEM OF THE ELEMENTS AND THEIR MAGNETIC PROPERTIES

The elements may be arranged in series according to the atomic weights in different ways. A certain periodicity between atomic weights and magnetic properties always appears. But if the atomic weights are represented by abscissæ and the magnetic susceptibilities as ordinates, the curve obtained is of a most irregular character, representing seven distinct maxima, among which that of the iron group is by far predominating. If only the sign of the magnetic properties is taken into account, one gets the best representation perhaps by the method of the helix due to B. K. Emerson, which is given in Fig. 1.

The strongly magnetic groups appear on a diameter, where we find Fe, Ni, Co, then Pd, Ru, Rh, then Gd, En, Sm, then Pt, Ir, Os. Moving on the spiral from iron to the right, we meet Mn and Cr, elements, which are paramagnetic, but whose strongly magnetic properties appear only in some of their alloys and compounds such as the Heusler alloys, mangenese-antimony, manganese-tin, manganese-zinc, Cr_5O_9. On the right-hand side from the ferromagnetic elements there are the paramagnetic elements; on the left-hand side, the diamagnetic elements. Opposite to the magnetic metals there are the inert gases, whose magnetic properties have not yet been determined. On the right-hand side of the inert gases we find the alkali metals, whose magnetic properties are not yet sufficiently known. Sodium and potassium seem to be paramagnetic. The strongly magnetic metals, cobalt, nickel and iron, belong to the elements with minimum compressibility, complex volume, with most complex spectra, with complex double salts, with great condensation of mass, the heavy metals. Thus it looks as if the condensation of electronic orbits were a maximum

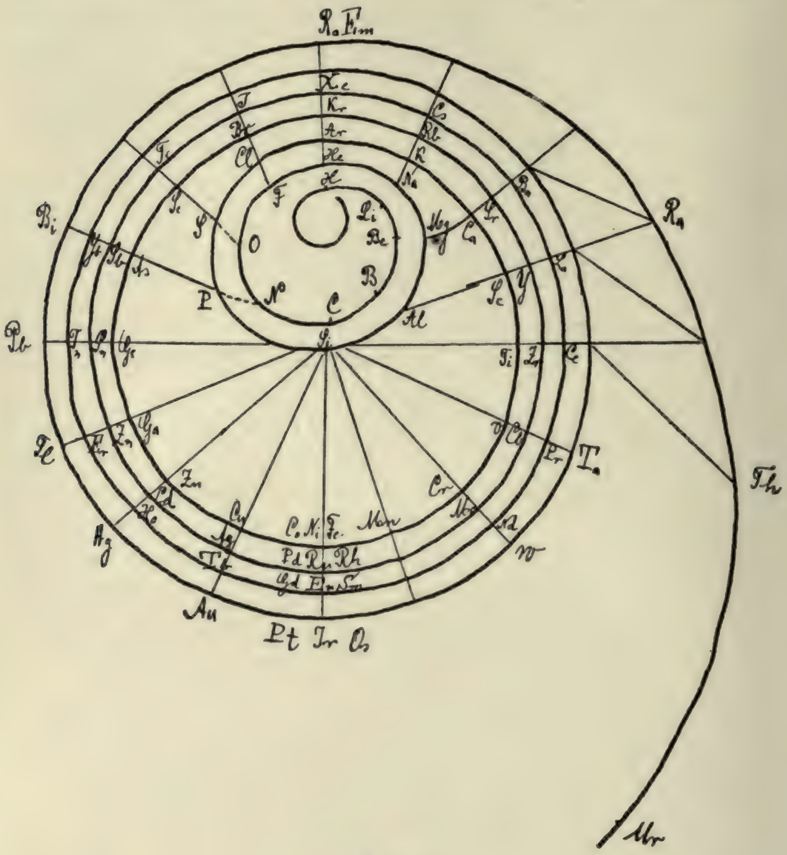

Figure 1

in these magnetic metals, and that the magnetic properties were related directly or indirectly to the mechanical and optical properties. But it is very remarkable that immediately after the strongly magnetic metals there follow the diamagnetic metals:

	k
Cu	−0.66
Ag	−1.4
Tb	......
Au	−2.6

On the next diameter we have

	k
Zn	-0.96
Cd	-1.16
Ho	......
Hg	-2.6

When we move outward on a diameter of the spiral, the diamagnetic susceptibility increases. The same rule is repeated by chlorine, bromine and iodine; sulphur, selenium, tellure; phosphorous, arsenic, antimony, bismuth. If a represents the atomic weight, α and β two constants, then the atomic susceptibility can be represented for the last three groups by:

$$\chi_a = -C_e{}^{\beta a - \alpha}$$

The same law seems to hold for all the groups of diamagnetic elements, which are in the previous representation on the left of the diameter passing through the iron group and the inert gases. Thus, for instance, for zinc, cadmium and mercury we have:

$$\chi_{Zn} = \frac{0.96 \times 65.4}{7.1} .10^{-6} = 8.83 \times 10^{-6}$$

$$\chi_{Cd} = \frac{1.16 \times 112.4}{8.6} .10^{-6} = 15.2 \times 10^{-6}$$

$$\chi_{Hg} = \frac{2.6 \times 200 \times 10^{-6}}{13.6} = 38.3. \times 10^{-6}$$

If we put

$$\chi_a = 10^{\beta_a + \beta}$$

where a is the atomic weight, we find from Cd and Hg for α and β the values:

$$\alpha = 0.6146$$
$$\beta = 0.00502$$

log $\chi_{Zn} = 1.583$, the calculated value $= 1.618$. The agreement is not so good for the last diamagnetic group of elements, Cu, Ag and An; here the atomic susceptibilities are as follows:

$$\chi_{Cu} = 5.29 \times 10^{-6}$$
$$\chi_{Ag} = 14.39. \times 10^{-6}$$
$$\chi_{An} = 26.55 \times 10^{-6}$$

The copper seems to make an exception. Whether this is due to an inaccurate determination of χ or to the fact that copper follows immediately after the iron group, remains an open question. Between the Zn, Cd, Hg group and the P, As, Sb group there are two more groups of diamagnetic elements; namely, those of Ga, Jn, Tl, and Ge, Sn, Pb. I find only the values

$$\chi_{Sn}=\frac{0.29\times119}{5.8}=5.9.10^{-6}$$

$$\chi_{Pb}=\frac{1.37\times206.9}{11.37}=25.0.10^{-6}$$

This agrees also with the general statement that along any diamagnetic diameter of the spiral the atomic susceptibility increases towards the periphery. It is an exponential function of the atomic weight.

If we travel along the spiral from copper towards zinc and from Ag towards Cd, we find the following values for the atomic susceptibilities:

Cu	5.29	10^{-6}	Ag	14.4
Zn	8.83		Cd	15.2
Ga	.....		In	.....
Ge	.....		Sn	5.95
As	5.8		Sb	77.5
Se	24.0		Te	38.9
Br	21.9		I	46.5

As and Sn are two decided exceptions to the rule that the atomic susceptibility increases from the south towards the north of the graphic representation.

While in the strongly magnetic metals the susceptibility decreases as we move on the diameter outward, we see here in the adjacent elements the diamagnetic susceptibility increases when we travel in the same direction. Oxygen again occupies an exceptional position through its magnetic properties. Its regular diamagnetic properties seem to appear only in some of its organic and inorganic compounds. Let us consider the gases:

O_2	CO_2	H_2O	NO	N_2	H_2
+	−	−	+	−	−

The + sign indicates paramagnetism the − sign diamagnetism.

It looks as if in free oxygen one of the atoms were in a different magnetic state than when it occurs in compounds. The same phenomenon occurs, for instance, in the ferricyanides, where the iron seems to have lost its magnetic properties, the ferridyanides being no more magnetic than salts not containing iron; even the combination FeO is very weakly magnetic. There exists a remarkable but very hidden relation between chemical and magnetic properties.

A modification of the theory of the difference between diamagnetic and paramagnetic properties will now be considered.

The phenomena mentioned in the previous paragraph seem to indicate that the magnetism is, as it were, due to revolving electrons on the surface of the atom, and that these electrons are connected with those forces which come into play in chemical reactions, in the optical phenomena and in mechanical properties. There appears to be no special reason why we should ascribe to all matter the diamagnetic rather than the paramagnetic property. Indeed, we may proceed in this way and assume that all matter is paramagnetic, each molecule having revolving electrons, with a resultant magnetic moment for an external point, so that the substance as such is paramagnetic. Let us further assume that there are nonrevolving electrons present which, while the external magnetic field is excited begin to revolve and revolve as long as the field lasts. These induced currents constitute the diamagnetic modification of the substance. If the resultant moment of these electrons is larger than that of the previously revolving electrons, then the substance is diamagnetic; if it is smaller than that of the previously revolving electrons, then the substance is paramagnetic. The fact that all substances have a line spectrum and that the lines are subject to the action of the magnetic field is not against this consideration. There is no evidence that the vibrating electrons, which produce the line spectra, are at the same time the revolving electrons of the magnetic properties. If an element like iron is very rich in emission lines then it may also contain a large number of revolving electrons, which produce the magnetic properties. In the elementary theory of the triplet and doublet in the Zeeman effect an electron is considered, vibrating in a given line under a certain angle with the direction of the magnetic field, this vibration is resolved in two components, one of which is parallel and the other perpendicular to the magnetic field; the light emitted in the direction of the lines of force is due to the perpendicular component of the vibration of the electron and consists of two circularly polarized beams. The transversal effect consists in three lines of plane polarized light. Now if we consider the light emitted not from a vibrating, but from an electron revolving in a plane perpendicular to the magnetic field, then we would see in the direction of the lines of force only the original line displaced, and if there be another electron revolving in the opposite direction in the same plane, then we would have the doublet of the longitudinal effect, as if there were only one electron vibrating.

The light emitted by a revolving electron in the transversal effect would be plane polarized, and if there were two electrons revolving in opposite directions, we would have plane polarized light also; and if there were an electron revolving in a circle whose plane coincided with the direction of the field, then its light emitted in the transversal direction would not be affected by the magnetic field, so that we finally have the triplet of the transversal effect. Thus we see that the simple case of the Zeeman effect can be explained either by one vibrating electron or by three revolving electrons. We can, therefore, not conclude that the revolving electrons which produce magnetic effects are at the same time those which are the sources of light. It is possible, but we have no proof as yet. At all events, the fact that the Zeeman effect occurs only in quasi abnormal states of matter as a consequence of ionisation, while the diamagnetism is a normal phenomenon, independent of ionisation, seems to point to the view that different electrons cause the two phenomena.

Let us consider an electron in equilibrium under the action of a system of electrical forces, but able to revolve in an orbit under the electrical forces induced during the establishment of an external field. Let: T be the final time of revolution,

E the electrical force acting on the electron,

e the charge,

m the mass of the electron,

ϕ the magnetic flux crossing the area A of the circle,

r the radius of the orbit,

v the final velocity,

ΔM the increase of the diamagnetic moment per unit volume,

N the number of such orbits per unit volume, then we have

$$-\frac{d\phi}{dt}=2\pi rEe$$

$$-d\phi=2\pi rEedt;\ mdv=eEdt$$

$$-d\phi=2\pi rmdv$$

$$\phi=2\pi rm\int_{o}^{t}dv=2\pi rmv.=H\pi r^2$$

$$v_1=\frac{Hr}{2m};\ T=\frac{2\pi r}{v_1}=\frac{4\pi m}{H}$$

$$\Delta M=N\Delta m=NAi=NA\frac{e}{T}=\frac{Nr^2eH}{4m}$$

By definition, the diamagnetic susceptibility *k* is given by

$$\Delta M=kH$$

Comparing the last two equations, we have:

$$k=k_2=\frac{Nr^2e}{4m}$$

In the previous theory we had:

$$k_1=\frac{N}{2}\frac{e^2r^2}{m}$$

In the modified theory, therefore, we have to assume that the radii are very small in comparison with what they would be in the older theory, and that N, the number of diamagnetic electrons, is small. In this case the difference between diamagnetic and paramagnetic elements would mainly depend on the kinetic energy of the electrons. If the kinetic energy of rotation is large we have paramagnetic substances; if it is small we have diamagnetic elements.

On the basis given above, P. Langevin worked out the kinetic theory of paramagnetic gases and found that the susceptibility *k* should be inversely proportional to the absolute temperature. This would be the theoretical demonstration of Curie's rule. But Dubois and Honda state that only palladium foil on heating followed more or less Curie's law, and showed complication on cooling. Moreover, Fe, magnetite, nickel, cobalt above the critical temperature seem to follow this simple law. Other ferromagnetic substances, such as phrrhotite above the critical temperature, behave in a very peculiar way. The kinetic theory of the paramagnetic properties can not, without modification, be extended to the liquid and solid state, because here the neighborhood of other atoms and the crystalline structure must have an influence on the magnetic properties of the molecules. This appears very distinctly from the measurement of Dubois and Honda.

IV

FERROMAGNETISM

P. Weiss has shown that the ferromagnetic properties can be described in an exceedingly simple way, namely, by the assumption of an intrinsic or molecular magnetic field which is in every point proportional to the intensity of magnetization. And in spite of the discrepancies between Langevin's kinetic theory and experimental results, Weiss found that the relation between the absolute temperature and the saturation value of magnetization holds over a wide range of temperature in the case of magnetite, for smaller ranges only in Fe, Ni and Co. At lower temperatures there are very considerable discrepancies again between temperature and magnetization. But the most convincing proof of the existence of the molecular field of Weiss exists in the variation of the specific heat in the neighborhood of the critical temperature. There must be a good deal of truth in the intrinsic molecular field. I have in an article published in the Physical Review, March, 1910, page 359, tried to calculate the absolute magnetic moments of the elementary magnets of iron, nickel and magnetite. The equations applied were those given by Weiss' theory:

$$a = \frac{mNT}{rT}$$

$$\frac{T}{Tm} = \frac{a}{3}$$

which is true for the absolute temperature Θ, where the spontaneous magnetization disappears.

$$a = \frac{mNTm\ a}{3rT} \text{ or}$$

$$m = \frac{3r\Theta}{NTm}$$

This calculation of *m*, the moment of the elementary magnets presupposes that the theoretical temperature relation holds from the critical temperature down to the absolute zero.

The values taken and the results are contained in the next table.

TABLE 1

Substance	Tt=20	Tm	Θ	N	NT=Hm	$m10^{20}$	$\mu_H 10^{24}$
Fe	1860	2120	756	3,850	6,560,000	5.15	1.66
F_3O_4	430	490	5362	33,200	14,300,000	2.02	0.93
Ni	500	570	376	12,700	6,350,000	3.65	4.8
Co	1421	1435	1075	6,180	8,870,000	6.21	3.24
Heusler Alloy	.....	518	310	12,940	6,700,000	3.55	1.60

The values for cobalt are taken from a thesis of W. W. Stifler[1] the values for Heusler alloy from a thesis of P. W. Gumaer.[2] μ_H is the mass of a hydrogen atom. If we divide 4.8 by 3 we find for this fundamental quantity 1.6, if we divide the value of cobalt by 2 we find 1.62, the average value of μ_H being $1.5 \cdot 10^{-24}$; $\frac{e}{\mu_H} = 9654$ thus $e = 1.45 \cdot 10^{-20}$. This value agrees well with that due to Rutherford. Thus the magnetic properties give an indirect method of determining this fundamental quantity of nature. This fact seems to me also to go to support the theory of Weiss of the intrinsic magnetic field. One further assumption has been made in this calculation, which is very important:

$a = \frac{mNT}{rT}$, where *r* is determined in the kinetic theory of gases by the following equation:

$$rN_1T = p$$

N_1 is the number of molecules of a gas in unit volume under the pressure *p* and at the temperature T. *r*T is twice the kinetic energy of a molecule corresponding to one degree of freedom. By extending this equation to the magnetic molecules of ferromagnetic metals, we assume that these molecules have the same degrees of freedom of rotation as the molecules of a gas. If we do this we come to the conclusion that the magnetic molecule of iron consists of 2, that of nickel of 6, and that of cobalt of 4 atoms.

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[1] W. W. Stifler, Phys. Rev. v. 33, p. 268, 1911.

[2] P. W. Gumaer, Phys. Rev. 1912.

V

THE MAGNETON OF P. WEISS

From recent magnetic investigation at very low temperature and at temperatures above the critical one, P. Weiss, in a number of articles published in the Comptes Rendus and in the Journal de Physique, has drawn another conclusion, which is confirmed by further investigations, means a fundamental progress in our knowledge of nature.

The molecular moments of magnetization were determined at the temperature of liquid hydrogen. P. Weiss gives the following values:

For iron,	12,360
For nickel,	3,370
For cobalt,	10,042
For magnetite,	7,417

If we divide the first number by 11, the second by 3, the third by 9 and the last by 6, we find 1123.5, thus iron cobalt and nickel have a common divisor, while magnetite seems to deviate considerably. P. Weiss calls this value the magneton-gram. Above the critical temperature the magnetite follows Curie's rule over certain intervals of temperature.

If σ_m represents the magnetic moment of the gram-molecule, its maximum value at absolute zero, then Langevin's theory of paramagnetic gases gives:

$$\frac{\sigma_m}{\sigma_{mo}} = \text{Aga} - \frac{1}{a}$$

where

$$a = \frac{\sigma_{mo} H}{rT}$$

By developing $\text{Aga} - \frac{1}{a}$ in a series and neglecting every term besides the first, we get:

$$\frac{\sigma_m}{\sigma_{mo}}=\frac{a}{3}=\frac{\sigma_{mo}H}{3rT};\ \chi_m=\frac{\sigma_m}{H}=\frac{\sigma_{mo}^2}{3rT}$$

and Curie's constant is equal to:

$$C_m=\chi_m T=\frac{\sigma_{mo}^2}{3r} \tag{1}$$

$r=83{,}155.10^6$ ergs per degree,
or, writing the equation for unit mass:

$$C=\frac{m\sigma_o^2}{3r}$$

If χ and $\frac{1}{T}$ are represented graphically, there appear four or five straight lines, giving five values for the constant C; this can be explained either by the assumption that *m* or *r* varies, or two or three quantities together. P. Weiss shows that the variation of *m* alone does not explain the observations, but that these constants may be correlated by the assumption that σ_o varies abruptly from one value to the other in very simple ratios. But it is surprising that with increasing temperature the magnetic moment per unit mass should increase in the ratio 1:1.25:1.5:2:2.5. In Langevin's original theory the magnetic moment is independent of the temperature; here it appears to increase in regular steps abruptly. But on the básis of the theory of Langevin which has as yet no direct experimental support, we may also assume that the degrees of freedom vary more or less abruptly so that Curie's constant increases with increasing temperature, or *r* decreases

$$rT=\frac{2L}{n}\ .$$

where *n* is equal to the number of degrees of freedom. If *r* decreases with increasing temperature, we see that the number of degrees of freedom *n* increases, and this seems to me much more probable than the increase of the magnetic moment with rising temperature; the molecule of F_3O_4 is complicated enough to allow at higher temperature an increase of the degrees of freedom.

P. Weiss supplies afterwards equation (1) to dissolved paramagnetic substances. Still considering the underlying diamagnetism of Langevin, and assuming that the diamagnetic atoms in the compounds with paramagnetic substances conserve their diamagnetism, P Weiss corrects the value of Pascal and finds corrections amounting to from 1 to 6%.

TABLE 2

Substance	$X_m 10^6$	σ_{mo}	$n=\frac{\sigma_{mo}}{1123.5}$	n′	n″
K and NH_4 ferricyanide	1,730	11,700	10.41	10	1.04
Fe and NH_4 pyrophosphate	7,990	24,600	21.89	22	2.19
Fe and NH_4 citrate	8,040	24,680	21.96	22	2.19
Na—Ferripyrophosphate	9,660	27,100	24.04	24	2.40
Na—Ferrimetaphosphate	13,000	31,500	28.03	28	2.8
Ferrichloride	13,100	31,390	27.93	28	2.8
Ferrisulfate	15,200	33,800	30.09	30	3.0
K—Ferrometaphosphate	11,300	20,200	25.99	26	2.6
Na—Ferrooxalate	12,300	30,480	27.11	27	2.7
Na—Ferropyrophosphate	13,000	31,370	27.91	28	2.8
Ferrosulfate	12,900	31,120	27.69	28	2.8

If we displace the decimal point by one cipher to the left, we
have for *n:* a series of values which is a little more deviating
1.04 from integers than Weiss' value But it would be
2.19 interesting to see the values without that doubtful
2.19 correction. If this series were correct, the magneton
2.40 gram in these substances would be ten times larger
2.8 than in the ferromagnetic metals. If we displace
2.8 the decimal point in the other direction we find an-
3.0 other common divisor of σ_{mo}, which would make the
2.6 magneton ten times smaller than in the iron, nickel
2.7 and cobalt. After the introduction of that doubtful
2.8 correction, P. Weiss finds among 27 substances meas-
2.8 ured by Pascal only 17 for which the agreement is sat-
isfactory. This is a little more than half of the salts chosen.

The theory of Langevin is furthermore extended to magnetic salts in the solid state. The results are given in the following

TABLE 3

Substance	$X_m 10^6$	σ_{mo}	$n = \frac{\sigma_{mo}}{1123,5}$	n″
$FeCl_3$	14,650	32,400	28.83	2.88
$FeCl_3 2NH_4ClH_2O$	12,830	30,330	26.99	2.69
$FeF_3 3NH_4F$	14,820	32,660	28.94	2.89
$FeF_3 2NH_4F\ H_2O$	14,965	32,800	29.19	2.92
$FeF_3 3H_2O$	7,899	32,860	21.23	2.12
Ferriacetylacetonate	10,922	28,150	25.05	2.50
Mn_3O_4	5,730	20,190	17.97	1.80
Cl_rCl_3	7,027	22,510	20.04	2.00
Cobaltacetylacetonate	7,767	23,730	12.12	2.11
$\frac{1}{2}\ Cr(NH_3)_6Cr(Cr_2O_4)_2 3H_2O$	7,080	22,650	20.16	2.00
$\frac{1}{2}\ Cr(NH_3)_4C_2O_4Cr(NH_3)_2(C_2O_4)_2 3H_2O$	7,080	22,650	20.16	2.00

Here it is much more interesting to displace the decimal point towards the left by one cipher. We find the following values:
2.88 a series which agrees, with one exception, even better
2.69 with whole numbers than that of Weiss. By these
2.89 common divisors the magneton gram would be ten
2.92 times larger than in the strongly magnetic metals.
2.12 Above the critical temperature the strongly magnetic
2.50 metals seem to follow Curie's rule, and from these
1.80 constants Weiss found again a common divisor, which
2.00 is very satisfactory for nickel and cobalt, unsatis-
2.11 factory for iron without the assumption of polymeri-
2.01 salions. Pure nickel at high temperatures has 8
2.01 magnetons; at the limit of the nickel iron alloys it
has 9, at very low temperatures 3, and in the solutions 16 magnetons. R. H. Weber[1] has given the susceptibilities of the salts of the iron group. Among nine or eight values only three show a well-defined common divisor. If magnetism can be broken up into magnetons as an electrical charge can be divided in electrons, it should be possible to isolate the magneton, as it was possible to isolate the electron.

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[1] Annalen der Physik, Vol. 36, p. 624, 1911.

Abstract

SOME PHYSICAL CONSTANTS OF SULPHUR TRIOXIDE. MELTING- AND BOILING-POINTS, DENSITY, COEFFICIENT OF EXPANSION AND MOLECULAR WEIGHT

By D. M. Lichty
University of Michigan, Ann Arbor, Mich.

Both the persistently liquid or α-sulphur trioxide and the ordinary solid or β-variety were investigated. The α-trioxide, prepared by carefully dehydrating ordinary oxide over phosphorus anhydride, melts at 16.79° (corr.) and boils at 44.88° under 760 mm. pressure. The melting- and boiling-points are generally given as 15° and 46°, respectively.

The density at intervals from 11.8° to 48° and the co-efficient of expansion between the same intervals are given in Table I.

Schultz-Sellak[1] found 0.0027 for the coefficient of expansion between 25° and 45°, and Schenck[2] 0.0023 between 11° and 35.3°.

The molecular weight of both the α and β-varieties, as calculated from the freezing-point depression of phosphorus oxychloride, is 80, as the data in Tables II and III show.

These results show that the α and β-varieties of sulphur trioxide behave essentially alike in phosphorus oxychloride, and have like molecular weights. The first column of molecular weights was calculated with K = 69, a value used by Oddo[3], the second column with 76.8, published recently by Walden.[4]

Oddo found that the molecular weight of the α-trioxide is 80, but that of the β-trioxide was 160.

It has also been found that, contrary to Schenck's[5] observation, the α-trioxide does not attain constant volume with unusual slowness when warmed or cooled to 35°.

[1] *Ber., 3,* 215.
[2] *Ann., 316,* 1.
[3] *Gaz. Chim. 31. II,* 141, 163, 165.
[4] *Z. anorg. Chem., 68,* 307–16.
[5] *Loc. cit.*

TABLE I

Temp.	Density	Coeff. Expan.
11.8°	1.9457	
		0.000676
15	1.9422	
		0.002005
20	1.9229	
		0.002204
25	1.9020	
		0.002363
30	1.8798	
		0.002466
35	1.8569	
		0.002671
40	1.8324	
		0.002754[1]
45	——	
		0.002805
48	1.7921	
11.8°–35°	——	
		0.002066
25°–48°	——	
		0.002665

TABLE II

Variety	Conc.	Depr.	Molecular Weights.	
β	0.817	0.731	77.07	85.80
β	1.479	1.343	76.00	84.61
β	2.154	2.019	73.60	81.94
α	2.902	2.796	71.63	79.85
α	3.637	3.595	69.79	77.69

TABLE III

α	0.882	0.813	74.82	83.30
α	1.540	1.435	74.08	82.28
β	2.297	2.214	71.57	79.68
β	3.152	3.139	69.28	77.13

[1] By interpolation.

Abstract

THE CONSTITUTION OF ALUMINATES

By Edward G. Mahin
Purdue University, LaFayette, Indiana

Aluminium and aluminium hydroxide dissolve in strong bases and it is at present believed that salts of a hypothetical "aluminic acid" (aluminium hydroxide ionized as an acid) exist in the solutions thus formed. A consideration of the properties of aluminium indicate a doubt as to the correctness of this view. Investigations of others are shown to be not entirely in harmony with the theory. In this paper is given an account of experimental work to determine (1) the heat of solution of aluminium hydroxide in sodium hydroxide, (2) the quantity of aluminium hydroxide precipitated from a sodium aluminate solution by a known weight of ammonium nitrate and (3) the relative weights of aluminium oxide and oxygen produced by the electrolysis of sodium aluminate. From the results obtained the author concludes that the colloidal character of aluminium hydroxide is a more important factor in conditioning its solubility in bases than is its amphoteric character. It is even doubted whether the substance is amphoteric at all, as this term is generally understood.

REPORT BY CHARLES MARIE IN THE NAME OF THE PERMANENT COMMITTEE OF THE INTERNATIONAL COMMISSION ON THE PUBLICATION OF ANNUAL TABLES OF CONSTANTS AND NUMERICAL DATA OF CHEMISTRY, PHYSICS AND TECHNOLOGY, APPOINTED BY THE SEVENTH CONGRESS OF APPLIED CHEMISTRY (LONDON, 1909).

Gentlemen:

If we were to give you in this report a detailed statement of the work and actions of the International Commission since the Congress in London, it would take too long, and we therefore ask you to allow us to condense the report into a statement of the most important facts.

A first general assembly of the Commission met in Paris in October, 1909, and delegated the necessary powers to administer the business of the Commission to a standing (permanent) committee, consisting of representatives of Germany, England, Holland and France (one from each of these countries), the representative of France being given the title and duties of General Secretary. This standing committee, to which later a representative of Italy was added, consists at the present moment of Professors M. Bodenstein (Hanover), Bruni (Padua), Ernest Cohen (Utrecht), Dr. C. Marie (Paris), and Dr. N. T. M. Wilsmore (London).

This standing committee, which was formed with the special purpose of rendering *meetings* of the committee *convenient*, held two meetings in 1910 and two in 1911; its last meeting was held in March, 1912, after the publication of the first volume.

This first volume of Annual Tables, which we present to the Congress, will tell you, better than any person could, what the work of the International Commission has been; it is not for us to pass judgment on this work. We must, however, call your attention to the importance of the work: it will constitute for everybody a revelation of the amount of work being done in the laboratories of the world! This very fact is in itself a demonstration of the usefulness and need of the work that has been done. Thanks to the Annual Tables we feel sure that everything in the domain of physics and chemistry, pure and applied, which may be expressed in numbers, will be catalogued. The value of this systematic work of organization has, further, received a first consecration by the recognition of the International Association of Academies.

Such an undertaking could be conducted only at a great cost, and you will find appended to this report, advisedly kept brief, a statement of the financial position of the Commission, which acknowledges gratefully all the generous contributions that made it possible for the Commission to meet the heavy expenses it was obliged to incur. Governments, Academies Scientific and Industrial Societies, private individuals, solicited by members of the International Commission, have hitherto furnished the sums necessary for the undertaking.

Unfortunately, as the value and importance of the volume just published demonstrate the usefulness of this publication in a most striking manner, so also has the *estimated cost* of publication been far *surpassed.* Those among you who received the first subscription blanks in October (1911), will remember that we promised to our subscribers a volume of at least 300 pages; we have published a volume of 766 pages! Our expenses consequently were increased, and in the same proportion, whereas the price of the volume was not changed. We do not know, as yet, how the work done will be judged in the world of science and of industry; we only know that the principle of the Tables must have been considered important, since the call, alone, for subscriptions, was answered by more than 800 subscribers, and we have, on the basis of this number, decided on the printing of 2000 copies; we may expect that this will be barely sufficient.

However, under the most favorable circumstances and without counting the losses incidental to commerce, it is impossible to obtain a sufficient revenue to pay the annual expenses from the sale of the volume at the price it is offered. It would be necessary, in order to obtain such a return, to effect the sale of more than 3000 copies or to increase decidedly the price of the volume.

The latter course could not be followed, excepting on a small scale; it would entail the risk of shutting out, at once, a large number of would-be buyers, and would, at all events, be a dangerous experiment. The sale of larger numbers appears to us as more likely, but can only gradually be attained; it is therefore indispensable that the International Commission receive endowments and contributions in order to continue its work.

We trust that you will recognize the intense effort involved in the work already accomplished and that you will give us the necessary authority to obtain the indispensable financial support which the work demands.

For the International Commission, the Permanent Committee:

Professor BODENSTEIN,
Professor BRUNI,
Professor ERNEST COHEN,
Dr. N. T. M. WILSMORE,
Dr. CHARLES MARIE,
General Secretary.

Paris, June 15, 1912.

TABLES ANNUELLES DE CONSTANTES ET DONNEES NUMERIQUES DE CHIMIE DE PHYSIQUE ET DE TECHNOLOGIE

COMITE INTERNATIONAL DE PUBLICATION

Etat général des Recettes et Dépenses arrêté au 10 mai 1912

RECETTES (Détail p. 2-6)

	Francs	
1909-1910	22.761,46	
1911	20.276,54	
1912	13.353,10	
Intérêts du Compte de dépôt	60,95	
		56.452,05

DEPENSES (Résumé ci-dessous)

	Francs	
1909-1910	20.306,50	
1911	15.561,05	
1912	14.368,25	
	50.235,80	
En caisse au Crédit Lyonnais	6.070,55	
En caisse au Secrétariat	145,70	
		56.452,05

Le Secrétaire général Trésorier:
C. MARIE.

SUBVENTIONS

Résumé des Recettes (Détail p. 2 et suiv.)

	1910 Francs	*1911* Francs	*1912* Francs
Allemagne	614,25	4.163,00	3.808,80
Autriche	6.915,36	1.651,95	1.669,95
Belgique	27,00	1.651,95	100,00
Danemark	27,00	100,00	100,00
Empire Britannique	2.468,75	2.011,20	100,00
Espagne	2.468,75	400,00	100,00
Etats-Unis	1.549,00	776,40	100,00
France	5.750,00	6.800,00	4.499,90
Hollande	1.462,90	1.674,40	4.499,90
Hongrie	1.462,90	1.674,40	2.090,00
Japon	150,00	150,00	150,00
Norvège	150,00	557,49	150,00
République Argentine	150,00	557,49	200,00
Roumanie	150,00	300,00	200,00
Russie	2.674,50	300,00	200,00
Suède	626,20	142,10	43,20
Suisse	626,20	1.550,00	43,20
	22.237,96	20.276,54	12.861,85

Ensemble: 55.376,35

Report	55.376,35
Souscriptions perpétuelles (1910) Dr. L. Haitinger (Weidling) et (1912) Prof. v. Goldschmidt (Heidelberg) ensemble	1.014,75
Intérêts du compte de dépôt	60,95
Total des recettes au 10 mai 1912	56.452,05

Résumé des Dépenses (Détail p. 7 et suiv.)

	1909-1910	*1911*	*1912*	*Totaux*
Secrétariats nationaux (Détail p. 7)	9.821,20	13.173,05	3.703,25	26.697,50
Collaborateurs extracteurs (Détail p. 9)	10.485,30	2.388,00 (1er semestre)	....	12.873,30
Tabulateurs (Vol. I)	....	....	10.665,00	10.665,00
	20.306,50	15.361,05	14.368,25	50.235,80

DETAIL DES SUBVENTIONS

Reçues par le Comité international depuis le début jusqu'au 10 mai 1912

Les subventions sont placées dans la colonne de l'année où elles ont été *versées* au Compte du Comité.

Pays	*Nom des Donateurs*	*1910* Francs	*1911* Francs	*1912* Francs
Allemagne.	Deutsche Bunsen Gesellschaft	614,25		
	Industrieller Verein Mulhausen		100,00	
	Königliche Akademie der Wissenschaften zu Berlin		1.232,00	

Pays	*Nom des Donateurs*	*1910* Francs	*1911* Francs	*1912* Francs
Allemange.	Schimmel u. C° Miltitz bei Leipzig........		616,00	615,00
	Chemische Fabrik, Griesheim-Elektron, Frankfurt a. Main..........		616,00	615,00
	Königliche Sächsische Gesellschaft der Wissenschaften-Leipzig...			368,40
	Verein deutscher Eisenhüttenleute..........		123,00	122,80
	Siemens u. Halske, Siemens-Schuckert-Werke (Berlin)......		615,00	614,00
	Allgemeine Elektrizitäts-Gesellschaft (Berlin)..		615,00	614,00
	Bergmann Elektrizitäts-Werke (Berlin).......		246,00	245,60
	Verein deutscher Ingenieure................			614,00
		614,25	4.163,00	3.808,80[1]
Autriche.	Verein österreichischer-Chemiker.........	104,70		104,35
	Kaiserliche Akademie der Wissenschaften in Wien..............	6.287,66		
	Osterreichischer Ingenieur u. Architektenverein (Wien)......		73,20	
	Gouvernement Autrichien		1.578,75	1.565,60
	Chemische physikalische Gesellschaft (Wien).	523,00		
		6.915,36	1.651,95	1.669,95
Belgique.	Mr. W. Spring (abandon d'honoraires)	27,00		
	Société chimique de Belgique.............			100,00
		27,00		100,00
Danemark.	Société chimique de Danemark........		100	100
			100	100
Empire Britannique.	J. Brown, Esq., F.R.S. (Belfast)..........	79,25		
	The Rt. Hon. the Earl of Berqueley, F.R.S...	1.258,00		
	Royal Dublin Society...	250,00	252,50	
	Royal Irish Academy...	125,50		

[1] *Allemagne.*— Deutsche chemische Gesellschaft.— Par suite d'un retard dans la transmission la subvention de cette société en 1912 (500 Marks) ne figure pas sur cette liste.

Pays	*Nom des Donateurs*	*1910* Francs	*1911* Francs	*1912* Francs
Empire Brittanique.	British Association for the Advancement of Science	756,00	753,60	
	Chemical Society		252,40	
	Royal Society of Edinburgh		126,15	
	Society of Chemical Industry		251,50	
	Faraday Society		126,20	
	Royal Society of Canada		248,85	
		2.468,75	2.011,20	
Espagne.	Académie royale des Sciences (Madrid)		250,00	
	Société espagnole de Physique et de Chimie		150,00	
			400,00	
Etats-Unis.	American Academy of Arts and Sciences	1.290,00		
	American Electrochemical Society	259,00		
	American Chemical Society		776,40	
		1.549,00	776,40	
France.	Association des anciens élèves de l'Ecole de Physique et de Chimie	100,00	100,00	
	Société chimique de France	500,00	500,00	500,00
	Association française pour l'avancement des Sciences	500,00	500,00	
	Société Industrielle de l'Est	100,00	100,00	
	Société d'Encouragement pour l'Industrie nationale	1.000,00	1.000,00	
	Association des Chimistes de Sucrerie et de Distillerie	50,00		
	Société française de Physique	500,00	500,00	
	Gouvernement français	3.000,00	3.000,00	2.999,90
	Société de Chimie-physique (Paris)		100,00	
	Académie des Sciences		1.000,00	1.000,00
		5.750,00	6.800,00	4.499,90

Pays	*Nom des Donateurs*	*1910* Francs	*1911* Francs	*1912* Francs
Hollande.	Congrès néerlandais pour les Sciences exactes et médicales	522,45	523,25	
	Institut royal des Ingénieurs à la Haye (Section d'Electrotechnique)	209,00	209,30	
	Société d'Utrecht pour les Sciences et les Arts	522,45	523,25	
	Société pour l'avancement des Sciences (Amsterdam)	209,00	209,30	
	Société chimique néerlandaise		209,30	
		1.462,90	1.674,40	
Hongrie.	Gouvernement			2.090,00
				2.090,00
Japon.	Chemical Society (Tokyo)	100,00	100,00	100,00
	Scientific Agricultural Society	50,00	50,00	50,00
		150,00	150,00	150,00
Norvège.	Nansenfond (Christiania)		557,49	
			557,49	
République Argentine.	Sociedad cientifica Argentina			200,00
				200,00
Roumanie.	Laboratoire d'acoustique et d'Optique (Bucarest)		300,00	200,00
			300,00	200,00
Russie.	Gouvernement russe	2.674,50		
		2.674,50		
Suède.	"Jernkontoret" (Stockholm)	274,65		
	Studentengesellschaft (Upsala)	351,55		
	Souscriptions diverses receuillies par M. le Docteur L. Ramberg (Lund)		142,10	
	Kemistsamfundet (Stockholm)			43,20
		626,20	142,10	43,20

Pays	*Nom des Donateurs*	*1910* Francs	*1911* Francs	*1912* Francs
Suisse.	Société de Physique et d'Histoire naturelle de Genève.........		100,00	
	Société Suisse de Physique		100,00	
	Sté de Chimie du Haut-Rhin.............		50,00	
	Gouvernement Suisse...		1.000,00	
	Société Suisse de Chimie.		100,00	
	Société de Chimie de Genève...........		100,00	
	Société Vaudoise des Sciences naturelles..		100,00	
			1.550,00	

DETAIL DES DEPENSES DU COMITE INTERNATIONAL

Depuis sa création (juin 1909 jusqu'au 10 mai 1912)

1°—Dépenses des Secrétariats nationaux

	1909–1910 Francs	*1911* Francs	*1912* Francs
Allemagne........................	1.181,45	1.019,30	au 10 mai 1911[1]
Autriche...........................	71,40	365,15	
Danemark.........................	......	217,75	
Empire Britannique...............	1.693,55	984,55	
Espagne............................	400,00	......	
Etats-Unis.........................	131,95	188,00	
France (Secrétariat Général) (Détail feuille 8).....................	5.475,70	9.493,25	3.703,25
Hollande...........................	497,40	238,00	
Italie...............................	139,45	341,10	
Japon..............................	4,65	4,85	
Norvège............................	......	50,55	
Russie..............................	......	75,10	
Suède...............................	18,90	195,45	
Suisse..............................	206,75		
	9.821,20	13.173,05	3.703,25

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[1] Les dépenses des Secrétariats nationaux pour le 1er semestre 1912 ne seront connues que plus tard.

DETAIL DES DÉPENSES DU SECRETARIAT DE PARIS

	1909–1910	*1911*	*1912*
	Francs	Francs	Francs 1 janvier à 10 mai
Frais de bureau	631,15	193,35	42,85
Impressions	826,65	3.663,65	643,20
Secrétaires adjoints	2.800,00	3.700,00	1.666,00
Collaborateurs temporaires[1]	115,50	783,25	717,00
Frais de poste	535,05	819,45	229,50
Dépenses diverses	567,35	233,55	404,70
	5.475,70	9.493,25	3.703,25

FRAIS D'EXTRACTION DES PERIODIQUES

	1910	*1911*	*1912*
	1er et 2e semestres	*1er semestre*	*2e semestre*
	Francs	Francs	Francs
Allemagne	4.146,00	577,00	126,00[2]
Autriche	558,00	97,00	
Belgique	27,00	......	
Danemark	....	32,00	
Etats-Unis	721,00	338,00	
Empire Britannique	2.100,00	776,00	
France	808,30	......	
Hollande	727,00	......	
Hongrie	....	79,00	
Italie	672,00	135,00	
Japon	48,00	......	
Russie	372,00	134,00	
Suède	179,00[3]	94,00	
Suisse	127,00	......	
	10.485,30	2.262,00	126,00

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[1] On comprend sous ce titre les honoraires attribués pour des travaux spéciaux (Traductions-Organisation de la souscription au premier volume, etc.).

[2] Cette somme représente un versement anticipé fait à deux collaborateurs — L'ensemble de ces dépenses d'extraction du 2e semestre 1911 sera règlé avant le 30 juin; il s'élève à la somme de 6300 francs environ.

[3] Cette somme représente l'extraction dans les pays scandinaves qui, depuis 1911, sont représentés au Comité international par des délégués différents.

THE VAPOR PRESSURES OF SOME CONCENTRATED ZINC CHLORIDE SOLUTIONS

BY ALAN W. C. MENZIES AND HENRIK BOVING
Oberlin College, Oberlin, Ohio

The measurements of vapor pressure here described became necessary, for the purposes of another investigation, when it was found that the data required were absent from the existing literature.

Qualitative analysis of the zinc chloride[1] employed showed the essential absence of impurities other than traces of sulphate and of arsenic. Quantitative analysis of a very concentrated solution for zinc and for chlorine indicated the quantity of basic salt present as 1.23% reckoned as Zn (OH) Cl. After addition of the calculated quantity of hydrochloric acid required to convert this to normal salt, solutions containing 60, 65 and 70 parts of $ZnCl^2$ per 100 parts of solution were prepared by suitable dilution.

The vapor pressures were measured by means of tensimeters of the Bremer-Frowein type, with oil as manometer fluid and phosphorus pentoxide as drying agent. In order satisfactorily to evacuate the tensimeter without the danger of concentrating the zinc chloride solution under investigation, the bulb containing the latter was immersed in a mixture of alcohol and solid carbon dioxide contained in a Dewar vessel. By means of a mercury pump it was then easy to reduce the pressure, before sealing off, to a few hundredths of a millimeter, as registered by a MacLeod gauge.

In measuring rather low vapor pressures by this method, the chief source of error lies in the presence of permanent gases that escape slowly from the substances in the tensimeter. For this reason, the oil and the zinc chloride solution were freed as far as possible from air beforehand. As it is not possible, however, entirely to avoid dissolved gases, since these may enter during the process of charging the tensimeter, it is necessary to have recourse to a process of equalizing the gas pressure on opposite sides. If the volume of the bulbs is very large in comparison with that of the manometer tube, and if the pressure of permanent gas is but small, this may be effected satisfactorily by placing the tensimeter in a horizontal position, thus putting the opposite sides in communication, and again erecting. In order that the permanent gas should distribute itself uniformly throughout the apparatus when in the horizontal position, it was found essential that all appreciable water vapor be removed from the apparatus by placing the bulb containing the solution, which was suitably bent back for this purpose, in a mixture of alcohol and solid carbon dioxide for two and a half hours. Otherwise the permanent gas on the side of the solution was invariably more humid than that on the side of the phosphorus pentoxide, and the distribution of permanent gas consequently unequal. To insure that the actual pressure of permanent gas was small, each tensimeter was re-exhausted after having been set up for several days. Absence of an uneven distribution of permanent gas was confirmed by the readings remaining identical after many days, during which the temperature had been varied in both directions; and also by constancy of reading after the tensimeters had again been placed in the horizontal position.

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[1] This was the "chemically pure" product of Baker and Adamson.

The tensimeters were immersed in a glass-sided water tank thermostat, constant by automatic regulation to two hundredths of a degree, and reached equilibrium within one hour. The temperature measurement, made by thermometers standardized by means of the transition point of Glauber's salt to anhydrous sodium sulphate and also by indirect comparison with the Sèvres standards, is believed accurate to a few hundredths; while the pressure measurement is believed accurate to 0.1 mm. of mercury.

VAPOR PRESSURE OF ZINC CHLORIDE SOLUTIONS

Parts per 100 parts solution	Pressure in mm. mercury at 0°,		
	14.64°	24.64°	29.60°
60	4.4	8.1	10.8
65	2.5	5.0	6.9
70	1.4	2.9	4.1

CONTRIBUTIONS A L'ETUDE DES SAVONS

Par Prof. Dr. A. Reychler
St. Nicholas (Waas) Belgium

I. La cristallisation des palmitates acides de sodium

Les recherches que j'ai faites sur le sujet indiqué par ce premier sous-titre ont été décrites dans le fascicule jubilaire de la Société Chimique de Belgique (mai 1912), de sorte qu'il suffira d'er rappeler ici les conclusions.

Les solutions étendues de palmitate de sodium commencent à cristalliser à une température qui, d'accord avec les indications de Krafft,[1] est comprise entre 47° et 37°, et qui cet d'autant plus élevée que la concentration saponine est plus forte. Le processus a ceci de particulier qu'il s'avive d'une manière très prononcée à quelques degrés au dessous de l'apparition des premiers cristaux, et qu'il s'achève presque intégralement en un petit intervalle de température.

Lorsque la normalité des solutions est assez élevée (de 0,05 à 0,02), les premiers cristaux sont nettement reconnaissables au sein d'une liqueur transparente, et la cristallisation pent être qualifiée de *nette en milieu limpide.*—Lorsque la normalité est inférieure à 0,02 les solutions sont plus ou moins troubles à haute température, et manifestent un châtoiement caractéristique un peu en deçà de 50°. Leur cristallisation se prononce vers 43° à 37°, et produit un enchevêtrement de cristaux trés fins: elle est *confuse en milieu trouble.*—Les solutions les plus étendues (de normalité 0,0025 par exemple) donnent des agglomérats presque grenus, très aptes à former dépôt.

Nos constatations résultent non seulement de l'observation directe des phénomènes, mais aussi de l'étude de la conductivité électrique des systèmes considérés. Cette conductivité diminue à température descendante, et signale par une chute rapide la période de cristallisation relativement active.

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[1] D'après Krafft, *Ber. d. D. chem. Ges. 28*, 2571, la température de cristallisation serait toujours voisine de 45°.

Il est à remarquer enfin que tous les systèmes étudiés ont accusé aux basses températures (de 30° à 18°) des conductivités tellement voisines, que les courbes représentatives en arrivaient à se confondre.

Les eaux-mères des différentes cristallisations étaient donc probablement de composition très semblable.

II. Les eaux-mères des palmitates acides

Dans une série de publications très intéressantes, Krafft et ses collaborateurs ont mis en lumière la relation qui existe entre la composition de certains savons acides et la concentration des milieux qui leur ont donné naissance.

[1]Au sujet du palmitate de sodium il nous apprend qu'une solution d'un gramme de savon neutre dans telle quantité d'eau dépose du savon acide renfermant tel pour-cent de sodium; et il assure en même temps que l'eau-mère de la cristallisation ne retient qu'une trace absolument négligeable d'acide gras. Mais il ne nous dit rien quant au degré d'alcalinité de l'eau-mére, ni quant au rendement en savon acide. L'omission paraît regrettable et demande réparation.

Lorsqu'une *mole* (278 gr.) de palmitate sodique donne la quantité équivalente d'acide libre, les diminutions corrélatives de la teneur en sodium et du poids de la matière organique sont de 8,27% et de 22 grammes. Lorsque toutefois la transformation n'est que partielle et s'arrête à la production d'un sel acide renfermant encore S% de sodium, les diminutions sont de $8{,}27-S\%$ et de 22 $\frac{8{,}27-S}{8{,}27}$ grammes.—L'acidification partielle *d'un gramme* de palmitate fournirait donc $1-\frac{22(8{,}27-S)}{8{,}27\times 278}$, c'est à dire 1—0,00957 (8,27—S) gr. de savon acide.—Or, la quantité de sel neutre contenue dans ce produit est proportionnelle à S. Elle se chiffre par $[1-0{,}00957\ (8{,}27-S)]\frac{S}{8{,}27}$ grammes et représente [1—0,00957(8,27—

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[1] F. Krafft et A. Stern, *Ber. 27*, 1747; Krafft et H. Wiglow, *Ber 28*, 2566.—Autres mémoires de la même série: *Ber. 27*, 1755; *28*, 2573; *29*, 1328 et 1334; *32*, 1584 et 1596.

$S)]\,\frac{1000S}{8{,}27\times 278}$ *millimoles.* Et comme notre matière première, un gramme de savon neutre, valait approximativement 3,60 millimoles, il faut que 3,60—0,435 S [1—0,00957(8,27—S)] millimoles de savon se soient dédoublées en acide libre, combiné à la masse cristalline, et en base libre, demeurée dans la liqueur-mère.

L'application de ce calcul aux données expérimentales de Krafft conduit aux déductions qui se trouvent groupées dans notre *tableau I.* Or la dernière colonne de ce tableau nous apprend une chose très importante: elle nous dit, en effet, que *la concentration de la soude dans les liqueurs-mères* commence par décroître en même temps que la concentration globale des systèmes considérés, mais *tend à devenir constante dès qu'elle est descendue à une valeur voisine de 0,002 millimole par centimètre cube.*[1]

TABLEAU I. (*Un gramme de palmitate de sodium*)

	Savon acide				Liqueur-mère	
Eau dissolvante	S	Poids calculé	Teneur en:		Soude	Concentration de la soude
			Soude	Acide		
Gr.	%	Gr.	Millimoles		Mmoles	Mmoles par $cm.^3$
200	7.01	0,988	3,01	3,60	0,59	0,00295
300	6,84	0,986	2,93	3,60	0,67	0,00223
400	6,60	0,984	2,82	3,60	0,78	0,00195
450	6,32	0,981	2,70	3,60	0.90	0,00200
500	6.04	0,979	2,60	3,60	1,00	0,00200
900	4.20	0,961	1,77	3,60	1,83	0,00203

La similitude de composition des eaux-mères fournies par des solutions diluées de palmitate de sodium se trouve donc annoncée par deux moyens d'investigation (titres I et II de ce mémoire). Pour confirmer le résultat de notre enquête nous avons estimé qu'il était nécessaire de *compléter l'étude analytique de nos systèmes diaphasés.*

[1] Les indications de Krafft concernant quelques cristallisations de stéarate, d'élaidate et d'oléate de sodium se prêtent á des déductions semblables aux précédentes, et démontrent également que la concentration de la soude dans les liqueurs-mères ne varie qu'entre des limites assez étroites (de 0,0028 à 0,0015 millimole par centimètre cube).

A cet éffet nous nous sommes servi de deux palmitates approximativement neutres, préparés à partir de sodium, d'alcool et d'acide palmitique pur (fusible à 62°,5). Le premier, que nous désignons par la lettre *A*, était faiblement acide et valait *par gramme* 3,543 millimoles de soude. Le second, que nous appelons *B*, représentait par gramme 3,592 mmoles de soude et 3,557 mmoles d'acide palmitique.

Tous les récipients employés étaient en verre d'Iéna ou en platine; et l'eau prise comme dissolvant était fraîchement distillée, et privée de CO_2 par quelques minutes d'ébullition. Quant au *mode opératoire*, il peut être brièvement indiqué de la manière suivante.

Une solution chaude l'environ 2 *gr. de palmitate* dans la quantité voulue d'eau est mise à cristalliser pendant trois jours, en fiole couverte[1]. Elle est ensuite filtrée à la pompe sur un disque de papier.

Le filtrat est pesé, afin que les données de son analyse puissent être rapportées à la totalité de la liqueur-mère. On le concentre éventuellement, et, après avoir ajouté à chaud une ou deux gouttelettes d'acide sulfurique, on laisse au *précipité d'acide gras* le temps de bien se former. Une simple filtration permet alors de séparer cet acide (destiné à être séché, repris par l'éther, isolé, pesé) d'avec un nouveau filtrat, dans lequel on dose *le sodium* à l'état de sulfate.

Le savon acide, séché sur assiette poreuse et dans le vide est pesé avec une approximation de ± 2 milligr. Pour l'analyser on en dissout une certaine quantité dans de l'eau chaude et on ajoute une dose non excessive d'acide sulfurique. L'ensemble est ensuite soumis à une série de changements de température, jusqu'à ce que *l'acide gras*, alternativement solide et fondu, finisse par surnager à l'état de fluide homogène. L'isolement et la pesée de cet acide n'offre aucune difficulté, non plus que le dosage du *sodium* dans la liqueur aquéuse.

Notre *tableau II* rend compte de deux séries d'expériences, dont les premières furent faites avec *le savon A*, les autres avec *le savon B*. La température finale des cristallisations fut de 18°,5 pour la *série A* et de 17° pour la *série B.* Toutes les données du tableau sont rapportées à l'emploi d'un gramme de palmitate. Les valeurs en soude et en acide sont exprimées en millimoles, et les concentrations en millimoles pour centimètre cube.

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[1] On psé successivement: savon, fiole + savon, et (après cristallisation faite) fiole + savon + eau.

TABLEAU II. (*Un gramme de palmitate de sodium*)

	Gr. d'*eau* par gr. de savon.	Savon acide				Liqueur-mère			
		Poids	Na	Valeur en:		Valeur en:		Concentration:	
				NaOH	Acide	NaOH.	Acide	NaOH	Acide.
		(Gr.)	%	(Millimoles)		(Millimoles)		(Mmoles par cm)^3	
Série A.				Trouvée		Calculée	Tr.		
1	46,87	0,976	7,785	3,3034		0,240	0,0159	0,0051	0,00034
2	95,09	0,963	7,673	3,2135		0,3295	0,0286	0,0035	0,00030
3	389,10	0,956	6,966	2,8970		0,646	0,153	0,0017	0,00039
Série B				Tr.	Tr.	Tr.	Tr.		
1	74,23	0,984	7,584	3,245	3,513	0,312	0,019	0,0042	0,00026
1 bis	77,07	0,985	7,57	3,242	3,522	0,342	0,019	0,0044	0,00025
2	122,06	0,977	7,63	3,242	3,486	0,339	0,035	0,0028	0,00029
3	243,8	0,966	7,49	3,146	3,445	0,442	0,088	0,0018	0,00036
4	435	0,936	6,85	2,788	3,377	0,785	0,1543	0,0018	0,00035
5	588,3	0,913	6,45	2,560	3,321	1,0225	0,2004	0,00174	0,00034
6	814,67	0,893	5,66	2,197	3,281	1,4167	0,2463	0,00174	0,00031

Pour la *sêrie A* la quantité de soude contenue dans les eaux-mères est calculée en tenant compte du poids et de la composition des savons acides. Pour la *série* B l'analyse complète du palmitate employé permet de faire le bilan des opérations analytiques, et de constater que la soude se retrouve presque intégralement, tandis que les dosages d'acide laissent un certain deficit (atteignant en moyenne 0,027 mmole pour l'ensemble d'un essai).

Les deux dernières colonnes du tableau II se rapportent à la composition des eaux-mères. Elles nous apprennent: 1° que la concentration de l'acide gras n'est pas négligeable mais prend une normalité voisine de 0,00035; et 2° que la concentration de la soude commence par être un peu forte (Série *B*, chiffres 0,0042 at 0,0028) mais accuse bientôt une tendance à devenir constante (chiffres 0,0018 et 0,00174). L'assurance donnée par Krafft concernant *l'absence* de l'acide gras dans les eaux-mères était donc pour le moins exagérée, mais *la grande similitude des phases liquides se vérifie parfaitement.*

Au point de vue de la mécanique chimique, il ne sera peut-être pas inutile de présenter la remarque suivante. Les solutions qui ont donné naissance aux systèmes *A3* et *B3, 4, 5 et 6* étaient toutes de normalité inférieure à 0,02, et doivent avoir cristallisé dans des conditions très semblables (d'une manière confuse, en milieu trouble et à partir d'une température assez basse). Or ce sont précisément ces mêmes solutions qui ont produit des eaux-mères de composition quasi constante. La coïncidence est de nature à faire supposer que les palmitates acides se sont formés par superposition de couches, le long d'un intervalle de température, et que ceux d'entre eux qui font équilibre à des eaux-mères à peu prés indentiques se trouvent probablement enrobés par des couches superficielles de composition peu variable.

III. L'extractibilité des solutions de palmitate et d'oléate de sodium par le toluol

Lors de la cristallisation d'une solution de palmitate l'acide ne peut se retirer du milieu aqueux qu'en entraînant une grande partie de la base présente. Mais les choses ne se présentent plus de la même manière lorsqu'on opère l'extraction de l'acide gras par quelque liquide semblable au toluol. La base alors ne prend aucune part à l'exode, mais reste dans la phase aqueuse tout en y devenante de plus en plus libre. Dans ses expériences de ce genre Krafft s'est complu à faire l'extraction quasi totale de l'acide palmitique par une série de traitements au toluol[1]. Nous avons touvé plus intéressant de mesurer l'effet produit par un traitement unique dans des conditions déterminées.

1. Essais d'orientation

A. Une solution d'un gramme *de palmitate de sodium* dans 700 gr. d'eau fut traitée, en fiole ouverte, par 200 centimètres cubes de toluol.

1° *A chaud* (vers 80°), en mélangeant les liquides par un mouvement giratoire.— Il s'est produit une émulsion très mousseuse, dont après refroidissement on a pu séparer 100 cm^3 de solution toluique. L'analyse de cette dernière a montré que l'extraction avait porté sur 0,624 gr. d'acide (68% de la quantité présente).

2° *A froid*, après cristallisation, en agitant le mélange.—Il y a eu production d'une suspension grossière, *non mousseuse*, et extraction de 0,07 gr. d'acide, c'est à dire de tout l'acide non engagé dans le savon cristallin.[2]

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[1] *Ber. d. D. chem. Ges. 27*, 1752; *28*, 2566.

[2] $0{,}00035 \times 0{,}256 \times 700 =$ près de 0,07.

B. Une solution *d'oléate de sodium* (1 gr. dans 700 cm^3 d'eau) a été traitée par 200 cm^3 de toluol.

1° *A chaud*, en agitant le mélange.—Emulsion mousseuse très stable. Après deux jours d'attente on a pu isoler 25 cm^3 de solution toluique. Extraction de 0,67 gr. d'acide (environ 70% de la quantité présente).

2° *A chaud*, en remuant prudemment les liquides avec une tige de verre.—Emulsion moins fine et mousse moins abondante. Extraction de 0,502 gr. d'acide.

3° *A froid*, en agitant la masse.—Emulsion très mousseuse, intraitable même après trois jours d'attente.

4° *A froid*, en remuant doucement avec une tige de verre.—Extraction de 0,207 gr. l'acide oléique.

L'efficacité du traitement dépend donc en grande partie du mode opératoire; mais d'une manière générale on peut cependant tirer les conclusions suivantes. Pour être *mousseuse* et abondamment *extractible* la solution de palmitate doit être prise à une température supérieure à sa période de cristallisation. La solution d'oléate est indubitablement dans le même cas; mais comme elle ne cristallise pas bien vite, elle reste mousseuse et extractible à basse température. Les deux propriétés marchent parfaitement d'accord, et semblant dépendre des mêmes conditions premières, notamment de la mobilité de l'acide gras et de la solubilité de cet acide dans le liquide extracteur.—*La mobilité* que nous avons en vue ne demande point que la solution de savon renferme une forte proportion d'acide hydrolytiquement libre, ou même des gouttelettes d'acide simplement émulsionné. Vu l'énormité du coefficient de partage[1] la moindre trace d'acide libre est presque intégralement enlevable, et comme le mécanisme de l'équilibre hydrolytique peut constamment régénérer cette trace, il n'est pas étonnant que l'extraction puisse atteindre un haut degré d'efficacité. Une circonstance doit cependant finir par mettre un terme au processus: c'est l'accumulation de plus en plus grande de soude libre dans la phase aqueuse.—Quant à *la solubilité dans le toluol*, elle est assez différente pour les deux acides dont nous avons utilisé les sels sodiques. Pour l'acide oléique elle est déjà illimitée à la température ordinaire, tandis que pour l'acide palmitique elle est petite à basse température et ne devient illimitée qu'au voisinage du point de fusion.

[1] L'acide gras libre est presque absolument insoluble dans l'eau.

2. Essais quantitatifs

Ceux-ci n'ont été faits qu'à froid (16°), et sur des solutions d'oléate de sodium. Le savon mis en expérience valait 7,41% de sodium et 92,90% d'acide oléique. Il représentait donc par gramme 3,2217 mmoles de soude et 3,2943 mmoles d'acide. Des solutions de cet oléate furent soumises à l'extraction toluique, et, pour que les traitements produisissent leur effet maximum tout en ne donnant que très peu de mousse. ils furent institués de la manière suivante.

On introduisait chaque couple de phases dans un assez long tube, et après avoir bouché ce tube on le disposait horizontalement. Tous les jours, pendant une semaine entière, on relevait plusieurs fois tantôt l'un tantôt l'autre bout du tube, de manière à déterminer un transport ondulatoire des phases superposées et un renouvellement des surfaces de contact. Le huitième jour on redressait le tube, et on en expulsait la très grande partie de la liqueur toluique en se servant d'un dispositif semblable à celui qui surmonte une pissette. Pour connaître la quantité de l'acide extrait, il suffisait ensuite de distiller une partie aliquote de la solution toluique, et de peser le résidu acide dans le ballon distillatoire même[1].

Notre *tableau III* rend compte des résultats ainsi obtenus. Il rapporte toutes choses à l'emploi de 50 cm³ de phase aqueuse (bien que nos essais 4a et 4c aient porté sur des solutions saponines deux fois plus volumineuses).

Tablcau III. (*Oléate de sodium a 7,41% de metal*)

	APRES EXTRACTION FAITE				Acide total (Mmoles)	% de l'extraction	Concentration de l'extrait (Mmoles par 50 cm³)
	Phase aqueuse		Phase toluique				
	50 cm³ valant NaOH (Millimoles)	Acide	Volume (cm³)	Acide extrait (Mmoles)			
1	3,335	3,262	50	0,148	3,410	4,3	0,148
2	1,667	1,566	50	0,139	1,705	8,1	0,139
3	0,834	0,713	50	0,139	0,852	16,3	0,139
3a	0,834	0,717	50	0,136	0,852	16	0,136
3b	0,834	0,732	30	0,121	0,852	14,2	0,202
4	0,417	0,286	50	0,141	0,426	33	0,141
4a	0,417	0,290	40	0,136	0,426	31,9	0,170
4b	0,417	0,306	30	0,121	0,426	28,4	0,202
4c	0,417	0,308	25	0,119	0,426	28	0,238

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[1] Toute pesée était précédée de la dessication de l'acide oléique dans le vide.—En aucun cas il n'a été nécessaire de filtrer la solution toluique.

Pour les essais *1, 2, 3, 3a* et *4,* mettant en oeuvre des volumes égaux des deux phases, la quantité de l'acide extrait reste constamment voisine de 0,14 mmole; et pour les autres expériences, où la dose de toluol se trouve réduite à 40, 30 et même 25 cm^3, le poids de l'extrait représente au minimum 0,12 mmole. L'acide gras est manifestement d'autant moins extractible que la phase aqueuse est plus riche en soude: *le pour-cent de l'extraction se montre inversement proportionnel à la concentration totale de la soude dans la solution saponine.*

L'interprétation plus approfondie des faits, au point de vue des lois de la mécanique chimique, rencontre de grandes difficultés. Si nous nous adressons aux essais les plus simples, et si nous admettons, par hypothèse, que la concentration de l'acide libre dans la phase aqueuse soit une fraction constante de 0,14, l'équilibre hydrolytique.

(Bioléate) Const. = (Base libre) (Acide libre)^2 demanderait qu'il y eût un rapport constant entre la concentration du bioléate et celle de la base libre. Or ce desideratum se vérifie approximativement pour les essais *1*, *2*, *3* et *3a*, mais pas du tout pour le N° 4.

	(Bioléate)	(Base libre)	Remarques
1	1,631	1,704	L'unité de volume est 50 cm^3. On met: (Bioléate) = *Acide non extrait* et: (Base libre) = Base total^2—bioléate. La concentration de l'acide libre est supposée constante et très petite.
2	0,783	0,884	
3	0,357	0,477	
3a	0,358	0,476	
4	0,143	0,274	

Il est donc probable que l'équation ci-dessus n'est pas seule à régler les phénomènes, et que déjà pour nos essais *3* et *4* la prépondérance de plus en plus prononcée de la base libre attribue un rôle de plus en plus important à l'équation.

(Oléate neutre) Const. = (Base libre) (Acide libre). Prise isolément cette dernière se montre absolument inapplicable.[1]

[1] Rien ne nous dit d'ailleurs que l'association moléculaire doive s'arrêter à la formation du bisléate, ni que la présence du toluol assure l'homogénéité réelle de la phase aqueuse.

Appendice

Il ne sera pas inutile d'intercaler ici quelques renseignements concernant la conductivité électrique des solutions aqueuses d'oléate de sodium.

Tableau IV. (*Oleate à 7,41% de sodium*)
Conductivités électriques, à la température de 18°.

Dilution (Litres)	Normalité alcaline.	Conductivité spécifique.	Conductivité moléculaire.	Remarques.
15	0,06670	0,001285	19,27	
30	0,03335	0,000689	20,67	
60	0,01667	0,000393	23,58	
120	0,00834	0,000234	28,08	Solution trouble.
240	0,00417	0,000160	38 40	Solution opalescente.
480	0,00208	0,000103	49,44	Solution légèrement opalèscente.
960	0,00104	0,000057	54,72	Solution légèrement opalèscente.
1920	0,00052	0,000032	61,44	Solution légèrement opalèscente.

Dans le *tableau IV* nous voyons que la conductivité moléculaire éprouve un accroissement anormalement fort entre les dilutions de 30 et de 960 litres; et nous remarquons en outre que cette conductivité est en général très petite (jusqu'à la dilution de 240 litres elle reste même inférieure au coefficient que l'on préverrait pour le seul sodium, abstraction faite de tout ion négatif). Nous déduisons de là: 1° que l'équilibre règnant est plus ou moins de nature hydrolytique, et 2° que l'oléate dissous paraît être partiellement formé de groupements plurimoléculaires, au sein desquels la mobilité des ions, y compris le sodium, se trouve gravement entravée.

L'extraction par le toluol, pratiqués d'après notre procédé quantitatif, a pour effet d'augmenter la conductivité spécifique de la solution soumise au traitement. Voici par exemple les chiffres trouvés pour une solution d'une mole d'oléate sodique dans environ 60 litres d'eau: 0,000416 après sept jours de conservation, et 0,000506 après sept jours de contact avec un demi-volume de toluol. Voici également les chiffres trouvés pour une solution deux fois plus diluée: 0,000250 et 0,000423.

IV. Le mécanisme du dégraissage

Nous avons vu qu'une solution de savon, prise à une température convenable, peut céder au toluol une grande partie des on acide gras, tout en gardant la totalité de son alcali. Et nous savons également que le système diphasé ainsi constitué n'a besoin que d'être dûment agité pour qu'il se transforme en une émulsion non dépourvue de stabilité.

La persistance de cette émulsion n'est pas difficile à comprendre. Lorsque la solution toluique d'acide gras se trouve divisée en globules microscopiques, les molécules acides doivent avoir une tendance à occuper la surface de ces globules, c'est à dire la place où elles peuvent s'allier au toluol par leur volumineux groupement hydrocarboné tout en présentant à la phase aqueuse leur côté CO_2H. Les globules acquièrent ainsi un revêtement de fonctions acides, par lesquelles ils peuvent entretenir des rapports de salification (compliquée de dissociation et d'hydrolyse) avec l'alcali du liquide baignant. Et comme cet alcali forme l'objet d'une répartition régulière, et qu'il sollicite de toutes parts les globules émulsionnés, il n'est pas étonnant que ces derniers soient tenus à distance les uns des autres, et empêchés de se réunir en formations plus massives[1].

La même interprétation s'applique aux opérations de dégraissage, domestiques ou industrielles. Lorsqu'une huile ou une graisse, finement étendue à la surface de fibres animales ou de quelque autre objet, se trouve mise au contact d'une solution d'oléate de sodium, *la matière grasse agit à l'instar d'un liquide extracteur* et soutire de l'acide à la phase aqueuse. La friction mécanique aidant, la souillure peut alors se résoudre en particules globulaires ou autres, enrobées de fonctions acides, et très aptes à s'émulsionner dans une liqueur aqueuse plus ou moins alcaline[2].

Il arrive d'ailleurs fréquemment que la souillure à enlever soit rance, ou même constituée en grande partie par de l'acide gras libre. Elle est alors de par elle-même capable d'entrer en relations avec de l'eau alcalinisée, de sorte que le processus de la mise en émulsion se trouve réduit à sa forme la plus simple[3].

[1] L'acidité des globules fait naître de l'affinité chimique entre les deux phases de l'émulsion. Elle diminue, comme on dit, la tension superficielle au contact des liquides hétérogènes.

[2] A la température ordinaire l'huile d'olives, par exemple, est miscible avec l'acide oléique.—Cette même huile ne prend une quantité illimitée d'acide palmitique qu'au voisinage de 60°, et par le refroidissement elle laisse cristalliser la très grande partie de la matière dissoute. Aussi les opérations de dégraissage ne sont elles pas indépendantes de certaines conditions de température.

[3] Comparer: F. G. Donnan, *Zeitschrift für Phys. Chemie, 31*, 42; *Chem. Centralblatt 1900, I*, 243.

Nos recherches sur le pouvoir extracteur du toluol nous ramènent ainsi à la théorie déjà proprosée par Chevreul, et remise au point dans les publications de Krafft: *le dégraissage ne consiste pas essentiellement en une saponification sodique ou potassique des souillures grasses, mais en une simple mise en émulsion.*

L'expérience de tous les jours nous apprend qu'un savonnage n'est efficace qu'à la condition d'être mousseux. La coïncidence devient compréhensible lorsqu'on admet, conformément aux indications de notre chapitre III, qu'une solution de savon n'est apte à développer de la mousse que lorsque son acide gras jouit d'un degré suffisant de mobilité et d'extractibilité.—Il convient d'ailleurs de tenir compte également des considérations que l'on peut tirer de certain théorème de Gibbs (Thermodyn. stud. 271), développé ultérieurement par d'autres auteurs, notamment par H. Freundlich (Kapillarchemie, 50). Dans la mousse l'alcali doit se localiser de préférence dans l'épaisseur des lames liquides, tandis que l'acide gras doit tendre à s'étaler sur les surfaces libres. La souillure grasse soumise à l'action de la solution mousseuse trouve ainsi l'occasion de s'incorporer de l'acide qui s'offre, pour ainsi dire, spontanément à l'absorption.

SOLUBILITY IN CASES OF ALTERED SOLID PHASE

By Arthur Rindell
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The agricultural chemist is very often consulted on the availability of the plant food in fertilizers, soils and other substances. While it is agreed, that the useful effect of such substances depends upon their solubility, the problem is to determine the contents which possess a suitable solubility. The usual methods for this purpose are unfortunately quite incorrect, because they are founded on the erroneous conception, that different concentrations of acids have specific solvent action. Having devoted my investigations to the removal of this difficulty, I have met with several others concerning the application of the solution-theory.

Most of the materials in question contain chemical compounds subject to hydrolysis, such as phosphates and silicates. Especially when the kation is able to form slightly soluble salts of more basic nature than the original compound we have secondary reactions leading to the formation of new solids. Because we have to make a solubility determination, the original matter must be present in excess while here the solid phase becomes altered and increased from one to two or more.

The solvents used are either water or dilute acids, mineral or organic. Moreover the neutrality (resp. acidity) of the solvent is altered simultaneously with the change of the solid and in a very different manner, according to the solubility of the hydrolysis products. Since the secondary reactions produce basic solids, the solution tends to contain relatively more of the anion, or anions, and to show an acid reaction. This corresponds to the case of the hydrolysis of salts of feeble bases with strong acids.

It is obvious that these circumstances produce a peculiar course in the act of solution, when to the same amount of solvent are added increasing quantities of the solid. In the case of an ordinary solution the concentration increases as a rectilinear function of the added solid until saturation is reached and then remains constant. When the solid phase is altered, the dissolving power of the solvent is diminished not alone by the increased concentration of the dissolved part, but also through the alteration caused by hydrolysis, and the solution curve shows a slightly inflected form with concavity towards the axis of X. This presents a maximum from which the slope downwards is very gradual when more solid is added.

In such cases there is no definite saturation and it is not easy to represent the solubility by a definite number, especially since the secondarily formed solids are for the most part colloids, whose absorptive power and other properties are slowly altered and thus cause new complications.

It seems to me very inconvenient and disturbing to count these cases as solubility phenomena, and I might appeal to the congress to accept a special term for the dissolution equilibria, where the solid phase is altered by hydrolysis, as indicated above. I would propose the words *solvable* and *solvability* in English, *lösbar* and *Lösbarkeit* in German and *solvable* and *solvabilité* in French.

Perhaps it is necessary to point out that this peculiar kind of equilibrium is of importance not only to the agricultural chemist. Important series of investigations concerning somewhat similar cases are shown for instance in papers of *C. Hoitsema*[1] on mercuric sulphate, of *G. Rutten*[2] and of *W. Hertz* and *A. Bulla*[3] on the nitrate of bismuth, of *J. M. van Bemmelen*[4] on the trichloride of antimony, and of *A. J. Cox*[5] on the chromates of mercury, bismuth and lead.

[1] Zeitschr. f. physikal. Chemie *17*, 651.
[2] Zeitschr. f. anorgan. Chemie *30*, 342.
[3] Zeitschr. f. anorgan. Chemie *61*, 387.
[4] Zeitschr. f. anorgan. Chemie *33*, 272.
[5] Zeitschr. f. anorgan. Chemie *50*, 226.

ON MIXED CRYSTALS OF POTASSIUM AND AMMONIUM CHLORIDES

BY KENJIRO UYEDA

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The formation of the mixed crystals of potassium and ammonium chlorides was first observed by Chevreul[1] and Knopp.[2] Their study was later taken up by Krickmeyer[3] who has shown among other things that their mutual solubilities are limited, and, further, Fock[4] has found a gap in their mutual solubilities at 25°, lying at about 18 to 99 mol. per cent ammonium chloride. At the suggestion of Professor Y. Osaka, I have been engaged in the further study of these mixed crystals, and the results are here briefly described.

The chlorides were purified by the repeated recrystallization, the flasks well steamed and the measuring apparatus carefully calibrated. Determination of the solubilities were made at 25.0°, 65.0° and 90.0°, the temperature in each case having been kept constant within 0.05°. They were conducted in the following way. Into an Erlenmeyer flask of about 25 c.c. capacity, about 5 grams of distilled water and sufficient quantities of the chlorides (in different proportions for the several determinations) were introduced, and the flask was closed with an India rubber stopper tightly covered, together with the neck of the flask, with a sheet of oil paper. It was shaken in a thermostat for a day and night, and then left to stand still. When the suspended matter settled down at the bottom of the flask, about 2 cc. of the clear solution were taken out and weighed, then diluted to 100 cc. with distilled water and subjected to analysis.

Ten cc. of the diluted solution were titrated for chlorine with decinormal silver nitrate solution using potassium chromate as an indicator. Ten cc. of the same solution were again taken

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[1] Compt. rend., *85*, 493 (1877).

[2] Molekularkonstitution und Wachstum der Kristalle, Leipzig, 1867.

[3] Zeit. f. physik. Chem., *21*, 53 (1896).

[4] Zeit. f. Kristall., *28*, 337 (1897).

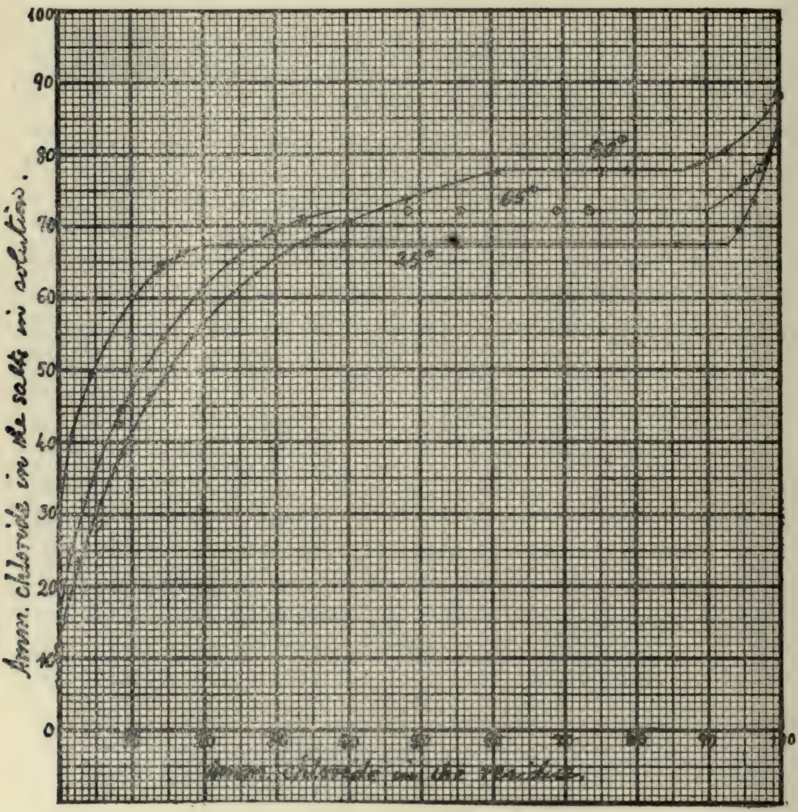

FIGURE I

in an Erlenmeyer flask of about 100 cc. capacity, and 20 cc. of the decinormal caustic potash solution were added. A small glass funnel was set at the mouth of the flask to prevent the loss of the liquid which was kept gently boiling, in order to expel ammonia completely from the solution. The latter was then allowed to cool, titrated for the free alkali with decinormal hydrochloric acid, and the amount of ammonium chloride calculated. From the amount of the total chlorine and of the ammonium salt, that of potassium chloride was estimated. The residue in the flask was analysed in the same way.

The results are given in the following table, and graphically shown in Fig. I.

25.0°		65.0°		90.0°	
I	II	I	II	I	II
10.4	0.	11.6	0.	23.7	2.7
26.9	0.	25.0	1.6	31.0	6.0
49.7	4.5	42.8	8.1	39.0	9.0
64.3	14.0	44.3	8.3	46.5	12.4
66.1	17.0	54.2	14.2	68.3	35.6
67.4	23.5	69.3	29.9	70.4	40.1
67.2	39.5	70.7	33.7	73.8	48.1
67.2	55.5	72.0	48.1	77.4	60.8
67.3	85.9	72.0	55.8	77.8	75.1
69.6	94.7	72.0	69.0	77.8	79.0
73.2	96.3	72.2	73.4	80.6	92.9
84.2	100.0	76.5	95.5	86.1	98.8
		77.9	97.3	88.8	100.0
		79.4	98.4		
		88.1	100.0		

In the table, the numbers in Column I represent in each case the gram percentage of ammonium chloride in the salts in solution, and those in Column II the gram percentage of the same salt in the residue.

From these results the following conclusions may be drawn:

I. The mutual solubilities of potassium and ammonium chlorides increase as temperature rises.

II. The solubility of ammonium chloride in potassium chloride increases with the temperature much more rapidly than that of potassium chloride in ammonium chloride.

III. The mixed crystals have the following gaps:

Temperature	Gram Percentage of Amm. Chloride	Molar Percentage of Amm. Chloride
25°.0	21-93	27-95
65°.0	38-90	46-93
90°.0	62-87	69-90

Abstract

EQUILIBRIUM IN THE SYSTEM OF SULPHURIC ACID, SULPHATE OF AMMONIA AND SULPHATE OF LITHIUM AT .30°C.

By Dr G. C. A. van Dorp
Katwijk aan Zee, Holland

The ordinary graphical figure in the equilateral triangle, scale one mm. for one per cent was not exact enough to elucidate the results of the analyses. The use of three perpendicular axes was necessary and a larger scale.

Besides the already known combinations of one mol. sulphuric acid to one mol. sulphate of ammonia and of one mol. sulphuric acid to one mol. sulphate of lithium I found three, as far as I know, as yet unknown combinations: 4 mol. sulphuric acid on three mol. sulphate of ammonia on one mol. sulphate of lithium; 4 mol. sulphuric acid on two mol. sulphate of ammonia on 2 mol. sulphate of lithium; 4 mol. sulphuric acid on 1 sulphate of ammonia on three sulphate of lithium. So the sum of the mol. in a combination in these three cases was found to be eight, which suggested the hypothesis that at 30° Celsius the combination possible with these components, also with less sulphuric acid were combinations of eight mol., a hypothesis which afterwards proved successful.

ON THE DETERMINATION OF THE WORTH OF TANNING MATERIAL, SPECIALLY FOR TANNING FISHING NETS

By Dr. G. C. A. van Dorp
Katwijk aan Zee, Holland

In the "Gedenkboek," offered to the late Dr. van Bemmelen, my highly esteemed initiator into the beauty of chemistry, and one of the founders of the colloid-chemistry, I published something of the above-named matter.

There had been sold at Katwijk a large fishing place at the Dutch coast, a tanning material which on hidepowder gave a better analysis than the ordinary cachou, and yet gave for the tanning of fishing nets very bad results. I then tried the adsorbing power of cotton for cachou and the other material (probably mangrove-extract) and found that cotton shaken with solutions of the first adsorbed a great deal of it, that of the second nearly nothing was adsorbed. This induced me to use no longer alone the hidepowder method, but also to determine the adsorbing power on cotton. I then used the same solution that had been used with the hidepowder and calculated the tanning worth in proportion to a standard material. This was but a preliminary method, as I did not doubt that the tanning material was not chemically bound by the cotton, but adsorbed according to the laws of adsorption. In this case there were two really exact methods, the first to determine once for all what under given conditions could be adsorbed out of a given solution of the standard material, and to determine in each case, how strong a solution of the material that was to be examined, ought to be to give the same adsorption. It was evident that in this manner as a rule more than one experiment was due, the first to know the probable strength of the solution, the second to try if this was really the right strength. Another method seemed to be to construct an adsorbing curve of the standard material. This curve once constructed, and the adsorption determined out of any solution of the material that had to be examined we could find in the curve the solution in the standard that would give the same adsorption, and so determine the value of the examined material.

So I resolved to determine such an adsorption-curve. This would have still more advantages, it would make me better acquainted with many of the properties of the procédé, which it was always good to know, and perhaps this knowledge would teach me the faults of the method, and the way how to diminish them. This proved true. First when starting from solutions of 7 gr. per L. I had hardly any difficulties, but when using a solution of 70 gr. per L. it appeared very difficult to determine what was adsorbed. The titration after Löwenthal was not well possible with the very colored solutions, and to dry such concentrated solutions into constant weight proved very difficult. In the drying over it was impossible at 100 centigrade, but at 103 centigrade it was possible, when the temperature was very exactly regulated to dry into constant weight. It was still better to dry in the vacuum at 100 centigrade. This strongly confirmed the truth asserted by those who, of late, advised to dry in the vacuum when using the official method of tanning analysis.

But even when drying in the vacuum constant adsorbing values were not found. It proved impossible to bring the adsorption to the end with shaking only. The solution decanted after half an hour's shaking from the cotton, and that pressed out of it, differed too much, shaking for a longer time would give no improvement. I then took refuge to a combination of shaking and pressing, at a fixed temperature, in wide-mouthed flasks, with an apparatus, reminding one of the old-fashioned Dutch churn. Thus I got results that agreed well with each other, when shaking for 5 minutes, pressing 2½ minutes, and repeating this three times. After this the mass would stand still, so that the foam could settle. Altogether the treatment would last three-quarters of an hour. To avoid differences, proceeding from differences in the preparation of the solution, it is recommendable to begin by making a very strong solution, out of which the more diluted are made.

In this way with my standard cachou I got the data given in Table I, with which the diagram was constructed. Now I must confess that this curve is not a real scientific, adsorption-curve.

Mathematical considerations, which to tell would take too long here, convinced me that it was impossible to test this curve on the adsorption formula, $\frac{K}{M}=kc^{\frac{1}{n}}$, this is only possible with solutions of chemically pure material, but I think that for my purpose the curve is very good. It is true that even so we cannot know how much real tanning material there is in a given solution (the adsorption being as is known, too much influenced by different additions), but we will know how much of it will be bound by the nets, and this is in the first instance the thing we want to know. Whether this method will also be of importance for the examination of tanning material used in leather manufacture is a thing I don't know, but I suppose it is worth trying.

Solved per Liter	Soluble in 50 c.c.		Rest in 50 cc. after 100 cc. was churned with 10 g.r. Cotton (corrected for the soluble part of the Cotton)	Adsorbed by Cotton
	Determined	Calculated		
70. gram	2.3670		2.1925	0.1745
49. gram	1.6604	1.6569	1.5013	0.1556
34.3 gram		1.1568	1.0307	0.129
27.4 gram	0.9286	0.9278	0.8173	0.1105
19.21 gram		0.6494	0.5663	0.0831
15.37 gram	0.5204	0.5195	0.4493	0.0702
10.76 gram		0.3636	0.3065	0.0571
8.61 gram		0.2908	0.2411	0.0497
6.88 gram		0.2326	0.1864	0.0462
4.81 gram		0.1628	0.1347	0.0281
3.85 gram	0.129	0.1302	0.1123	0.0179

DIE PRUFUNG VON LABORATORIUMTHERMOMETERN

GEHEIMER REGIERUNGSRAT PROF. DR. WISBE
Charlottenburg

Das Glasthermometer, besonders in seiner gebräuchlichsten Form als Quecksilberthermometer ist für den Chemiker eines der wichtigsten Hilfsinstrumente sowohl im Laboratorium wie im Fabrikbetriebe. Die Genauigkeit der Thermometer ist aber keine absolute, sondern nur eine relative, da es fast unmöglich ist, ein ganz fehlerfreies Thermometer herzustellen. Sie bedürfen daher stets einer Korrektionstabelle. Ausserdem unterliegt das Glasthermometer, wie viele andere Jnstrumente, beim Gebrauch Veränderungen, die von Zeit zu Zeit seine Nachprüfung nötig machen.

Der Chemiker ist aber meist nicht in der Lage, seine Thermometer selbst zu kontrollieren, auch stehen ihm die Erfahrungen, welche zu einer sachgemässen Prüfung nötig sind, in der Regel nicht zu Gebote.

Es ist daher von grossem Wert für den Chemiker, dass eine Reihe von staatlichen Anstalten bestehen, die sich mit der Prüfung von Thermometern befassen. Hierbei muss in erster Linie der Physikalisch-Technischen Reichsanstalt in Charlottenburg gedacht werden, da sie diejenige Anstalt ist, die sich am längsten und in umfangreichster Weise damit beschäftigt. Auch hat die Reichsanstalt ähnlichen Jnstituten in anderen Ländern in vielen Beziehungen zum Vorbilde gedient. Von den Anstalten in anderen Ländern seien nur die bekannteren aufgezählt, das Bureau of Standards in Washington, das National Physical Laboratory in Teddington und das Laboratoire d'Essais in Paris.

Diese Jnstitute haben für die Prüfung von Thermometern besondere Vorschriften herausgegeben, von denen die der Reichsanstalt die ältesten sind und die den Vorschriften der übrigen Länder als Vorbild gedient haben. Jn Deutschland befasst sich auch die unter Aufsicht der Reichsanstalt stehende Grossherzolich Sächsische Prüfungsanstalt in Jlmenau mit der Prüfung von

Laboratoriumthermometern. Jch will mich darauf beschränken, auf Grund der deutschen Prüfungsbestimmungen kurz die hauptsächlichsten Anforderungen anzugeben, die bei der Prüfung von Thermometern an letztere zu stellen sind und zwar mit besonderer Berücksichtigung der Laboratoriumthermometer.

Eine der wichtigsten Fragen für die Güte eines Thermometers ist die Beschaffenheit des Glases sowohl in chemischer wie in physikalischer Beziehung. Das Glas hat, wie viele andere Körper, die Eigenschaft der thermischen Nachwirkung, die sich durch das Ansteigen des Eispunktes bei neuen Thermometern dokumentiert. Man kann dieses jahrelang andauernde Ansteigen des Eispunktes vermeiden, wenn das Thermometer vor der Herstellung seiner Teilung einer künstlichen Alterungsverfahren unterzogen wird, das in einer 8 bis 10-tägigen Erhitzung des Thermometers auf einer Temperatur besteht, die der Erweichungstemperatur des Glases nahe kommt. Nach der Erhitzung muss eine möglichst langsame Abkühlung des Thermometers erfolgen.

Ein solchermassen behandeltes Thermometer erfährt bei nachherigem Gebrauch keine weitere Erhöhung, wohl aber nach jeder Erhitzung eine kleine vorübergehende Erniedrigung, eine Depression des Eispunktes, deren Grösse von der Höhe der Temperatur und von der chemischen Zusammensetzung des Glases abhängt. Glassorten, welche Kali und Natron enthalten, weisen grosse Depressionen auf, diejenigen mit nur *einem* Alkali kleine. Von den zur Herstellung besserer Thermometer bekannten Glassorten zeichnen sich die Jenaer Thermometergläser durch besonders kleine Nachwirkungen aus. Thermometer aus dem Jenaer Normal-Thermometerglas 16^{III} zeigen nach Erwärmung auf 100° nur eine Depression von 0,05 bis 0,07° C. solche aus Jenaer Borosilikatglas 59^{III} oder aus Jenaer Verbrennungsröhrenglas nur 0,02°.

Die Prüfung der Thermometer zerfällt in zwei Teile, die Vorprüfung und die Hauptprüfung. Erstere erstreckt sich auf die ordnungsmässige Herstellung des Thermometers, während letztere die eigentliche thermometrische Untersuchung umfasst.

Bei der Vorprüfung wird nachgesehen, ob die Kapillarröhre rein ist und ein gleichmäissg verlaufendes Kaliber hat. Am oberen Ende der Kapillare soll eine birnförmige Erweiterung angeblasen sein, um abgetrenntes Quecksilber leichter zu vereinigen und ein Zersprengen des Thermometers bei Ueberhitzung zu verhüten. Das Quecksilber muss rein und trocken sein, so dass beim Zurückgehen des Fadens an keiner Stelle der Kapillare sich Teilchen von ihm abtrennen.

Thermometer für Temperaturmessungen über 280° C. müssen oberhalb des Quecksilbers mit einem trockenen Gase (Stickstoff, Kohlensäure) von entsprechendem Drucke gefüllt sein, um das Quecksilber am Sieden zu hindern.

Die Skalenteilung soll ohne augenfällige Einteilungsfehler in dauerhafter Weise ausgeführt sein. Die Teilstriche sollen senkrecht zur Achse des Thermometers stehen. Besonderer Wert ist auf eine deutliche Bezifferung der Skala zu legen.

Die Hauptprüfung beginnt mit einer mindestens achttägigen Beobachtung der Thermometer hinsichtlich der Unveränderlichkeit ihrer Angaben durch Eispunktsbestimmungen oder dergl.

Die weitere Prüfung erfolgt sodann, je nach der Beschaffenheit der zu prüfenden Jnstrumente entweder durch eine Bestimmung des Fundamentalabstandes, durch Kalibrierung und Vergleichung mit Normalthermometern oder nur durch Vergleichung mit Normalthermometern in Temperaturbädern.

Als Temperaturskala wird allgemein die hundertteilige internationale Wasserstoffskala zu Grunde gelegt, die mit der thermodynamischen Skala fast identisch ist. Leider ist man bis jetzt nur zu einer Vereinbarung zwischen 0 und 100° gekommen, für höhere Temperaturen besteht noch keine vollkommene Einheitlichkeit. Es ist aber wenigstens so viel erreicht, dass man z.B. für den Siedepunkt des Schwefels, der bei thermometrischen Arbeiten auch als Fixpunkt benutzt wird, die Temperatur 444,7° C angenommen hat, die wahrscheinlich bis auf weniger als 0,1° mit der thermodynamischen Skala übereinstimmt.

Bei der fundamentalen Prüfung eines Thermometers sind auch die s.g. Gasreduktionen zu berücksichtigen. Jedes Glasthermometer zeigt die Temperatur in seiner individuellen Skala an, die von der Skala des Gasthermometers je nach der Art des Glases verschieden abweicht. Für die bekannteren Glasarten sind die Abweichungen ein für alle Mal durch umfangreiche Vergleichungen mit dem Gasthermometer bestimmt worden, so dass es leicht ist, die Angaben aller Glasthermometer auf dasselbe einheitliche Mass zurückzuführen.

Die zweite Art der Prüfung ist einfacher und geschieht durch Vergleichung in Temperaturbädern mit Normalthermometern, die an das Gasthermometer angeschlossen sind. Zur Vergleichung werden Flüssigkeits-oder Dampfbäder benutzt, für tiefe Temperaturen flüssige Luft sowie Gemische aus Salzen mit Eis oder aus Alkohol mit fester Kohlensäure.

Die Prüfung der Thermometer erfolgt im Allgemeinen so, dass die ermittelten Korrektionen sich auf ganz eintauchender Faden beziehen; auf Wunsch kann jedoch das Thermometer für eine bestimmte Eintauchtiefe geprüft werden; es ist in diesem Falle die mittlere Temperatur des herausragenden Fadens beim Gebrauch des Thermometers anzugeben.

Für die verschiedenen Gattungen von Thermometern sind bestimmte Fehlergrenzen vorgeschrieben, bei deren Einhaltung die Thermometer einen amtlichen Stempel als Kennzeicher der vollzogenen Prüfung und einen Prüfungsschein erhalten, in dem die ermittelten Korrektionen angegeben sind. Die Genauigkeit in den Angaben der Korrektionen richtet sich nach der Beschaffenheit der Jnstrumente und dem Ausfall der Prüfung und kann in sehr weiten Grenzen schwanken. Für Laboratoriumthermometer werden die Korrektionen in der Regel auf 0,1° C. bei hochgradigen Thermometern auf halbe oder ganze Grade abgerundet.

Diese wenigen Andeutungen mögen genügen, um zu zeigen, welch' grosse Mühe mit der sachgemässen Prüfung von Thermometern verbunden ist, zugleich aber auch, wie notwendig eine solche Prüfung ist, wenn es sich darum handelt, genaue Temperaturmessungen auszuführen. Jn Deutschland sind im vorigen Jahre 110000 Thermometer amtlich geprüft worden, unter denen sich über 7000 Laboratorium—und ähnliche Thermometer befanden, darunter allein 2000 hochgradige, zum Teil mit Temperaturangaben bis 575° C. Für die anderen Länder stehen mir die Zahlen nicht zur Verfügung, allein ich zweifle nicht, dass sie auch eine erklekliche Höhe erreichen. Eine besondere Genugtuung gewährt dabei die Gewissheit, dass durch die amtlichen Prüfungen dieser Thermometer in den verschiedenen Staaten nach gleichartigen Grundsätzen die Einheitlichkeit in den Temperaturangaben für alle geprüften Thermometer, besonders für die Laboratoriumthermometer, gewährleistet ist.

Schliesslich möge darauf hingewiesen werden, in welcher Weise die Verwendung ungeprüfter oder fehlerhafter Thermometer die Genauigkeit der Untersuchung beeinträchtigen kann. So ist z.B. bei der Bestimmung der Dichte mit Pyknometern eine Genauigkeit der Temperaturbestimmung auf 0,1° C. unerlässlich, um die dritte oder vierte Dezimale sicher zu erhalten. Bei feineren polarimetrischen Untersuchungen muss die Temperatur der zu untersuchenden Lösung mit mindestens der gleichen Genauigkeit bekannt sein. Auch dürften die grossen Abweichungen bei den in der Litteratur angegebenen Schmelzund Siedepunkten sich zum grossen Teil durch Verwendung fehlerhafter Thermometer erklären lassen.

THE SYSTEM OXALIC ACID, OXALATE OF AMMONIUM AND WATER AT 30° AND 45°

BY H. W. WOUDSTRA
Helder, Holland

We know three well-defined ammonium salts of oxalic acid:

1e. The neutral oxalate $(COONH_4)_2.H_2O$
2e. The acid oxalate $(COO)_2$ $H.NH_4H_2O$
3e. The quadroxalate $(COOH)_2(COO)_2$ $H.NH_4.2$ H_2O

The first crystallizes in long prisms, which are rhombic, hemiedric. Its solubility after Engel[1] is 2,215 grams in 100 grams water. On heating a solution of this salt in an open vessel ammonia is said to escape and prolonged boiling will leave behind a solution of pure oxalic acid (Gillot[2]).

The acid oxalate, too, crystallizes in rhombic crystals. The solubility of these salts has been determined with only moderated precaution as to constancy of temperature by William Ripley Nichols.[3]

In hundred grams of water of 15° dissolve 4.22 grams of the neutral oxalate; at 11°5, 100 grams of water dissolve 6.26 grams of the acid oxalate. The solid salt in equilibrium with the saturated solution at 11°5 has after Nichols the composition of the pure acid oxalate.

This last result does not agree with the experiments of Engel[4], who declares not to be able to determine the solubility of acid oxalate because this salt decomposes in solution into quadroxalate and neutral oxalate. The first salt separates from saturated solution of the acid oxalate. He worked at 0°.

The solubility of the quadroxalate, which crystallizes in the triklinic system as determined by Nichols, amounts to 1.81 grams in 100 grams water.

In this paper I have studied the equilibria, which occur when mixtures of oxalic acid and ammonium-oxalate in different proportions are shaken with water at constant temperatures in a thermostat. The temperature of the thermostat was kept nearly constant within 0.1° by means of a toluol-thermo-regulator. The well-stoppered flasks contained in most cases weighed quantities of the three components, water, oxalic acid and neutral oxalates. Equilibrium was reached within 2-10 days; each day the flasks were shaken for about 6-8 hours by means of a hot-air-motor which turned the axle in the thermostat, on which the flasks were fixed.

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[1] R. Engel. Comptes Rendus d. l'Acad. d. Sc. d. Paris, 102, 365.
[2] Gillot. Bulletin Acad. Roy. Belg. 1900, 744.
[3] W. R. Nichols. Chem. Nem. Vol. 21-22, p. 244, 1870.
[4] l.c.

The composition of a solution, which was in equilibrium with the solid phase, was determined in the following manner: a weighed quantity of the solution was titrated with chamæleon solution after addition of sulphuric acid, the total amount of oxalic acid in this way being estimated. Another weighed quantity was distillated with kalium-hydroxide; the ammonia set free was titrated with hydrochloric acid and bariumhydroxide.

The compositions of the solutions are given in Table I under B in percentages of anhydrous free oxalic acid, and neutral ammonium-oxalate for the temperature of 30°. Under A the compositions of the initial mixtures of water, oxalic acid and ammonium-oxalate are indicated in the same way.

Table II contains these compositions for a temperature of 45°. Fig. I represents the results of Table II graphically. The corners of the equilateral triangle A B C represent, respectively, water, anhydrous neutral oxalate and anhydrous oxalic acid. Each point within the triangle represents a mixture of these three components. The percentages are given by the distances of the point from the sides of the triangle, measured along lines parallel to the sides. To find the composition of the mixture represented by point E, f. i. we draw a line parallel to A C or B C. The distance of E from A B measured along one of these lines is equal to the percentage of anhydrous oxalic acid.

In the same way by drawing a line through E parallel to A C or B C, the distance of E from A C, measured along one of these lines represents the percentage of anhydrous oxalate.

The point E represents the quadroxalate, F the acid oxalate, G the neutral oxalate. The oxalic acid is represented by the point D on the side A C.

The isotherm at 45° MHIKL consists of four branches corresponding with the solid phases $(COOH)_2.2_2H_2O$, $(COOH)_2.(COO)_2$, $H.NH_4.2\ H_2O$, $(COO)_2\ H.NH_4.H_2O$ and $(COONH_4)_2.H_2O$. The solutions represented by the points of these four branches are respectively in equilibrium with these substances.

All points in the area AMHIKL represent unsaturated solutions; all points in the area MHIKL.BC supersaturated solutions, which decompose in saturated solution and solid phase.

The point N_1, f.i. represents such an unstable system, which separates into quadroxalate and the solution represented by the point N. The point which represents the solution in equilibrium with the solid phase is found by drawing a line through the points which represent the solid phase and the unstable system.

If the composition of two solutions in equilibrium with the same solid phase and the compositions of the unstable systems, which separated into these solutions and this solid phase, is known, the composition of the solid phase may be found by drawing lines through the points which represent the solution and the corresponding initial unstable system. The point of intersection of these lines represents the composition of the solid phase.

We see from the shape of the isotherm, that on adding neutral oxalate to the saturated solution of oxalic acid the concentration of the solution at first slightly increases; soon, however, tetraoxalate separates; the solution decreases constantly its amount of dissolved substances. As soon as the composition of the solution corresponds with a saturated solution of quadroxalate the concentration of the solution increases on further addition of neutral oxalate.

The solubility of the quadroxalate may be graphically determined by drawing the line E A. Its point of intersection with the isotherm represents the saturated solution of this salt. In this way we find for the composition of this solution: 3% anhydrous oxalate of ammonium and 6.3% anhydrous oxalic acid.

The amount of dissolved quadroxalate calculated from these data are respectively: 11.27% and 10.97%; mean, 11.12%. At 45° the saturated solution of quadroxalate of ammonium contains 11.12% $(COOH)_2\ (COO)_2\ H.NH_4.2\ H_2O$.

From the isotherm at 30°, which may be constructed after

Table I we deduce, graphically, that the saturated solution of quadroxalate at 30° contains 2% ammonium oxalate and 4% oxalic acid, which corresponds respectively with 7.52% and 6.90% quadroxalate; mean, 7.21%. The isotherm at 30° resembles very closely that at 45°.

On further increasing the amount of neutral oxalate the point I is reached. This ———————————— is a second tripelpoint, where solution, quadroxalate and acid oxalate coexist. This point falls at 45° and at 30° exactly on the line F A, which confirms the experiments of Engel. It is impossible to prepare a saturated solution of acid oxalate in equilibrium with pure acid oxalate. Some quadroxalate will always separate from the solution.

The solutions in equilibrium with pure acid oxalate contain more oxalate of ammonium than the saturated solution of acid oxalate. Their concentration increases gradually till the third tripelpoint K is reached. Here neutral oxalate separates. The solutions in equilibrium with neutral oxalate gradually decrease in concentration on further addition of neutral ammonium oxalate. When we begin with a saturated solution of this salt and add oxalic acid the concentration of the solution increases; more neutral oxalate goes into solution.

ABSTRACT

In this I determined:

1e. The isotherms of the system ammonium oxalate, oxalic acid and water at 30° (cor) and at 45° (corr);

2e. The solubility of oxalic acid at 30° and 45° respectively, 12.59 and 21.015 grams in 100 gram solution;

3e. The solubility of neutral ammonium oxalate at 30° and 45°, respectively, 5.53 grams and 8.3 grams in 100 gram solution;

4e. I proved that a saturated solution of acid ammonium oxalate deposes at 30° and at 45° quadroxalate of ammonium;

5e. I determined the solubility of quadroxalate graphically at 7.21 grams in 100 gram solution at 30° and at 11.12 grams in 100 gram solution at 45°.

TABLE I

A		B		Solid phase
Oxalate of Ammonium	Oxalic Acid	Oxalate of Ammonium	Oxalic Acid	
0.13%	20.58%	0.14 %	12.36 %	Oxalic acid
1.79%	18.27%	0.28 %	12.775%	id. + Tetra-oxalate
1.46%	19.48%	0.28 %	12.775%	id. id.
1.88%	20.31%	0.28 %	12.95 %	id. id.
0.27%	22.32%	0.285%	12.345%	id. id.
0.71%	19.42%	0.29 %	12.68 %	id. id.
0.97%	19.72%	0.29 %	12.74 %	id. id.
0.48%	19.76%	0.29 %	12.68 %	id. id.
1.37%	20.12%	0.29 %	12.51 %	id. id.
2.00%	19.28%	0.30 %	12.81 %	id. id.
0.37%	20.28%	0.30 %	12.71 %	id. id.
0.68%	11.11%	0.37 %	10.46 %	Tetra-oxalate of Ammonium
....	....	0.43 %	11.44 %	id.
1.13%	9.26%	0.47 %	8.87 %	id.
0.83%	16.30%	0.97 %	11.36 %	id.
10.03%	24.07%	0.91 %	5.65 %	id.
....	....	1.14 %	4.65 %	id.
....	....	3.60 %	3.55 %	id.
10.80%	20.67%	5.91 %	4.00 %	id.
....	....	5.96 %	4.17 %	Tetra-oxalate + hydro-oxalate
....	....	5.98 %	4.17 %	id.
13.87%	15.86%	5.98 %	4.23 %	id.
17.28%	14.10%	6.00 %	4.25 %	id.
....	....	6.21 %	4.08 %	Acid-oxalate
....	....	6.785%	3.56 %	id.
....	....	6.73 %	3.82 %	id.
....	....	6.015%	3.96 %	id.
26.38%	5.10%	8.19 %	3.36 %	Acid-oxalate + neutral oxalate
27.65%	4.28%	8.20 %	3.06 %	id.
20.37%	11.90%	8.24 %	3.31 %	id.
....	....	8.26 %	3.41 %	id.
23.38%	9.60%	8.27 %	3.49 %	id.
....	....	8.30 %	3.39 %	id.
24.14%	7.23%	8.32 %	3.22 %	id.
32.03%	2.75%	8.34 %	3.32 %	id.
27.28%	3.55%	8.36 %	3.30 %	id.
....	....	8.36 %	3.04 %	id.
20.37%	11.90%	8.40 %	3.34 %	id.
25.81%	7.53%	8.51 %	3.22 %	id.
....	....	8.52 %	3.25 %	id.
....	....	8.63 %	3.20 %	id.
....	....	7.40 %	2.76 %	Neutral oxalate
....	....	5.53 %	0.22 %	id.

TABLE II

A		B		
Oxalate of Ammonium	Oxalic Acid	Oxalate of Ammonium	Oxalic Acid	Solid Phase
....	....	....	21.01%	
....	....	....	21.02%	Oxalic acid
....	....	0.22%	21.22%	id.
....	....	0.25%	21.09%	id.
....	....	0.27%	21.22%	id.
0.24%	24.93%	0.27%	21.21%	id.
....	....	0.30%	21.32%	id.
....	....	0.31%	21.31%	id.
....	....	0.53%	20.73%	Oxalic acid and Tetra-oxalate
1.97%	23.63%	0.53%	21.44%	id.
....	....	0.53%	21.38%	id.
....	....	0.53%	21.46%	id.
....	....	0.53%	21.50%	id.
1.94%	26.39%	0.53%	21.30%	id.
0.65%	26.23%	0.54%	21.35%	id.
1.27%	24.24%	0.56%	21.23%	Tetra-oxalate
....	....	0.61%	20.55%	id.
2.58%	23.13%	0.54%	20.92%	id.
....	....	0.51%	20.88%	id.
3.91%	21.33%	0.79%	16.44%	id.
6.48%	21.22%	1.23%	12.28%	id.
9.46%	22.18%	2.16%	7.98%	id.
9.59%	24.37%	3.54%	5.83%	id.
11.08%	19.02%	5.65%	5.67%	id.
11.55%	18.56%	6.72%	5.95%	id.
13.46%	17.40%	8.77%	6.69%	Tetra-oxalate + acid-oxalate
15.12%	14.46%	8.72%	6.37%	id.
17.76%	12.63%	8.93%	6.27%	Acid-oxalate
16.00%	11.00%	9.04%	6.14%	id.
....	....	12.40%	4.97%	Acid-oxalate + neutral oxalate
23.32%	6.36%	12.27%	5.00%	id.
19.83%	7.93%	12.28%	5.02%	id.
19.99%	10.00%	12.37%	5.01%	id.
25.19%	2.64%	8.31%	3.04%	Neutral oxalate
25.00%	0.98%	9.59%	1.45%	id.

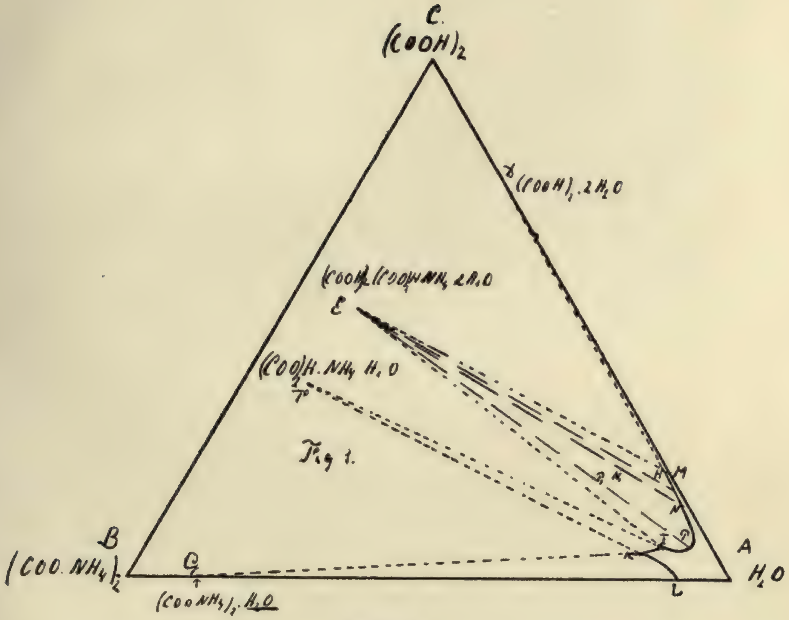
C.
$(COOH)_2$
D $(COOH)_2.2H_2O$
$(COOH)_2(COO)_2HNH_4\ 2H_2O$
E
$(COO)_2H.NH_4\ H_2O$
F
Fig 1.
H
M
N
P
I
K
L
A
H_2O
B
$(COO.NH_4)_2$
G
$(COONH_4)_2.H_2O$

FIGURE 1

Abstract

STUDIES ON THE CHEMICAL KINETICS OF CATALASE

BY EIICHI YAMASAKI

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The chemical kinetics of this important enzyme is complicated by the fact that it is destroyed with considerable rapidity in the presence of the substrutum, hydrogen peroxide. But as this substance can be measured with great ease and accuracy and the enzyme of well defined qualities can be readily obtained, the more detailed study of the subject seemed to afford a promising opening for kinetic investigation of the more complicated enzyme actions. According to Prof. Ikeda the course of decomposition of hydrogen peroxide by catalase can be described by the following extremely simple equations:

$$\frac{dc}{dt} = -kEc \quad (a) \quad \frac{dE}{dt} = -k'Ec \quad (b)$$

where c represent the concentration of the peroxide, E that of the enzyme, t time, and k and k′ the velocity coefficients. The author undertook the verification of these equations and was able confirm all the deductions experimentally. The enzyme employed in the experiments described in this paper was obtained from young shoots of bamboos, *Phyllotachys mitis, Riv.* The conditions of the experiment were varied with respect to temperature and concentrations of the substrutum and the enzyme. In all thirty four courses of the reaction were measured and calculated.

From (a) and (b) the following relation is obtained by integration and transformation;

$$v = k'(A + c) \qquad (c)$$

where v stands for the relative velocity of the reaction and A for

$$\left(\frac{k}{k'}E_o - C_o\right);\quad E_o \text{ and } C_o$$

being the initial concentrations of the enzyme and the substrutum respectively. V was calculated directly from the experimental data. On plotting the relation between v and c in a diagram, it was found that all the points belonging to a single course of the reaction lie on a straight line, and that all the lines pertaining to one and the same temperature are parallel to one another. In this way equation (c) was directly verified and (a) and (b) indirectly. By the graphical construction approximate values of k′ and A were obtained. The more exact values were then calculated by successive approximation from the integrated equation,

$$\ln\frac{C_o}{C} - \ln\frac{C_o + A}{C + A} = k'At$$

The determination of k′ in this way seems to be tolerably accurate, because all the values for the same temperature agree remarkably well among themselves. On the contrary, the values of kE_o calculated from that of A are not so concordant. But the proportionality between kE_o and the amount of the enzyme taken for the experiment was established beyond a doubt.

As a pure enzyme is an unknown thing, the concentration of an enzyme must always be expressed in an arbitrary unit. In the present investigation the unit was so chosen that at the standard temperature of 18° C. the value of k becomes unity. By a special series of measurement, in which the concentration of the enzyme remained the same while the temperature was varied, the temperature coefficient of k was determined. It was found to be 1.21 for 10°, a surprising small value, which proves that the velocity of the reaction is mainly determined by that of diffusion.

The temperature coefficient of k′ was found to be somewhat larger, *i.e.*, 1.40. With these temperature coefficients and the value of k′ at 18° C. it is possible to describe the course of reaction at any temperature and for any initial values of the concentrations of the enzyme and the peroxide. The equation for the purpose has the form:

$$C=\frac{(kE_0-k'C_0)C_0}{kE_0e^{(kE_0-k'CO_0)t}-k'C_0},\text{(d)}$$

or

$$C=\frac{C_0}{1+k'C_0t}\qquad\text{(e)}$$

In the cases where $kE_0-k'C_0>0$, the reaction proceeds to the complete disappearance of hydrogen peroxide, while in the opposite cases where $kE_0-k'C_0<0$ the reaction does not proceed beyond a certain value of C. When $kE_0-k'C_0=0$ equation (e) describes the course of the reaction. These equations were found fully adequate to represent the experimental results.

ZUR SYSTEMATIK DER KOLLOIDE

VON RICHARD ZSIGMONDY

Im Jahre 1903, zu einer Zeit, wo die Eigenschaften kolloider Lösungen noch sehr unvollständig bekannt waren, hat Arthur Müller[1] eine Einteilung der Hydrolsole in 2 Klassen vorgeschlagen, die fundamental von einander verschieden sein sollten. Zu der einen rechnete er die Metalle und Sulfide, die er als Suspensionen feiner Teilchen ansah, die andere, zu der er Lösungen von Stoffen wie Gelatine aund Eiweiss zählte, sprach er als Lösungen hochmolekularer Verbindungen an. Die Geringfügigkeit des osmotischen Drucks bei den letzteren betrachtete er als Folge des hohen Molekulargewichts der in Betracht kommenden normal gelösten Stoffe.

Wir wissen heute, dass kolloide Metalle bis zur optischen Homogenität zerteilt werden können, sich dann in optischer Hinsicht vollkommen wie krystalloide Lösungen von Farbstoffen verhalten; dass Gelatinelösungen, viele Eiweiss—und Farbstofflösungen oft ganz erfüllt sind von sichtbaren Ultramikronen, dass man Gelatine—Eiweiss—und andere Kolloidlösungen durch Kollodiummembranen, *die für Krystalloide vollständig durchlässig sind*, abfiltrieren kann, wie kolloides Gold, dass also in Bezug auf räumliche Diskontinuität zwischen den als "Suspensionen" und den als Lösungen bezeichneten Systemen kein wesentlicher Unterschied besteht. Eine rein molekulare Zerteilung, wie sie *Muller* allgemein für die letzteren angenommen hat, erweist sich nur als Spezialfall, der in wenigen, seltenen Fällen realisiert erscheint (z. B. beim Rinderhämoglobin nach Hüfner[2]).

Die Elektrolytempfindlichkeit, die Müller als charakteristisches Merkmal für die suspensoide Natur der Metallkolloide und ähnlicher Systeme ansieht, erweist sich gleichfalls als unzureichend, um einen Unterschied zwischen Lösungen und Suspensionen herauszukonstruieren. Es genügt ja ein *minimaler* Zusatz von Schutzkolloid, der die Viskosität des Systems in keiner Weise

[1] *A. Müller*, Z. anorg. Chem. *36*, p. 340 (1903).

[2] G.Hüfner, Engelmanns Archiv. f. Physiol. Physiol. Abt. *1894*, p. 130; (*1904*) p. 217; *1907*, p. 209.

erhöht, um eine Metallkolloidlösung ebenso elektrolytbeständig zu machen wie eine Eiweisslösung. Die Grösse der Metallteilchen wird durch diesen Zusatz nicht geändert, er genügt aber. um das Verhalten des Systems gänzlich zu ändern, die "suspensionsähnliche" Flussigkeit in eine "lösungsähnliche" zu verwandeln.

Die Theorie der Brown'schen Bewegung (Einstein[1]; v. Smoluchowski[2]) lässt voraussehen, dass auch den kolloiden Sulfiden, Metallkolloiden, etc., ein osmotischer Druck gegen ihr Filtrat zukommt, der, wenn störende Momente fehlen, der Teilchensahl proportional ist. Der Grund warum er sich meist der Messung entzieht, liegt in der Unmöglichkeit, die nur in grosser Verdünnung beständigen, *reinen*, schutzkolloidfreien Metallkolloide genügend weit zu konzentrieren. Bei As_2S_3—Solen haben Picton und Linder[3] tatsächlich osmotischen Druck nachgewiesen, Whitney und Blake[4] wie The Svedberg[5] konnten bei Gold Diffusion nachweisen[6].

Bei Kolloiden, die sich stärker konzentrieren lassen ohne dabei zu koagulieren, erreicht der osmotische Druck nicht nur messbare, sondern auch zuweilen ganz beträchtliche Höhen.

Also auch in bezug auf osmotische Eigenschaften ist ein prinzipieller Unterschied zwischen beiden Zerteilungsarten nicht zu machen.

Im Anschluss an A. Müller[7] und Bechhold[8] teilt Noyes[9] die Kolloide gleichfalls in 2 Gruppen, die "kolloiden Suspensionen" und die "kolloiden Lösungen", und kennzeichnet die ersten als nicht zäh, nicht gelatinierend und leicht durch Salze koagulierbar, die letzten als zähe, gelatinierend und durch Salze nicht koagulierbar. Statt des Ausdrucks "kolloide Suspensionen" sind zur Bezeichnung der oben charackterisierten Systeme noch mehrere andere vorgeschlagen worden: Hydrophobe Kolloide (Perrin), lyophobe Kolliode (Freundlich), Suspensionskolloide (Höber, Wo. Ostwald), Suspensoide (v. Weimarn) usw.; statt der Bezeichnung "kolloide Lösung" die Ausdrücke: Hydrophile, lyophile Kolloide, Emulsionskolloide, Emulsoide usw.

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[1] A. Einstein, Annalen d. Phys. (4) *17*, p. 549 (1905); *19*, p. 371 (1906). Z.f. Elektrochem. *14*, p. 235 (1908).

[2] M.v. Smoluchowski, Annalen d. Phys. (4) *21*, p. 756 (1906); 25, p. 205 (1908).

[3] H. Picton und S. E. Linder, Journ. Chem. Soc. *61*, p. 114 (1892).

[4] Whitney und Blake, Journ. of the Amer. Chem. Soc. *26*, 1361, 1904.

[5] The Svedberg, Zeitschr. f. physikal. Chem. *67*, 105, 1909.

[6] Es kann kaum einem Zweifel unterliegen, dass die relativ hohe Konzentration, die Blake bei seinem Gold erzielte, auf Anwesenheit von Spuren von Schutzstoffen beruhte, welche die Teilchenvereinigung verhinderten.

[7] A. Müller, Z. anorg. Chem. *36*, p. 344 (1903).

[8] H. Bechhold, Z. phys. Chem. *48*, p. 393 (1904).

[9] Arthur A. Noyes, Journ. of Amer. Chem. Soc. *27*, p. 85 (1905).

Es scheint bisher übersehen worden zu sein, dass eine Einteilung der Kolloide nach obigem Schema, da es viele Merkmale in Betracht zieht, underchführbar ist. Es gibt, z.B., "nicht zähe" und schwer durch Elektrolyte fällbare Kolloide, die in obiger Einteilung keinen Platz finden, so Paal's kolloides Silber. Kolloide Zinnsäure ist gelatinierbar, fällt aber leicht durch Elektrolyte, ist darum ebensowenig einer oder der anderen Klasse einzuordnen.

Einige der genannten Forscher haben die zahl der Merkmale noch vermehrt und damit die Einteilung nicht verbessert; durch die Ausdrücke "Suspensions"—und "Emulsionskolloide" werden Vorstellungen über den Aggregatzutand der zerteilten Materie fixiert, die keineswegs der Wirklichkeit zu entsprechen brauchen.

Für die folgenden Ausführungen ist noch auf eine Schwierigkeit hinzuweisen, die darin besteht, dass die Eigenschaften zäh, gelatinierbar und durch Elektrolyte leicht fällbar nicht eindeutig bestimmt sind. So hängt die Zähigkeit sehr von der Konzentration ab; Gallerten entstehen aus einem Sol zuweilen durch Temperaturänderung, zuweilen durch andere Einflüsse, und die Einteilung ändert sich je nachdem man unter "gelatinierbar" die Fähigkeit, Gallerten überhaupt zu bilden oder nur die Eigenschaft bei Temperaturerniedrigung zu gelatinieren versteht.

Die Elektrolytfällbarkeit endlich variiert in weitestem Masse je nach der Art der Elektrolyte, die in Betracht kommen. So braucht Albumin sehr viel Alkalisalz zu seiner Fällung, wird aber schon durch geringe Mengen Schwermetallsalze koaguliert.

In der folgenden Tabelle I können daher einige der angeführten Kolloide auch an eine andere Stelle gesetzt werden, falls man die Begriffe Gelatinierbar, etc., anders auffasst als ich. Durch geeignete Kombination der oben gegebenen Eigenschaften kann man zu folgenden 8 Klassen von Kolloiden kommen, und es ist nicht schwer, einen oder mehrere Repräsentanten für die Mehrzahl derselben zu finden.

TABELLE I

Klasse	*Eigenschaften*	*Beispiele*
1	Zäh, gelatinierbar, durch Elektrolyte schwer fällbar	Gelatine u. and.
2	Zäh, gelatinierbar, leicht fällbar	Graham's Caramel, Seifenlösungen, etc.
3	Zäh, nicht gelatinierbar, schwer fällbar	Dextrin, Grahams, koll. Wolframsäure
4	Zäh, nicht gelatinierbar, leicht fällbar	
5	nicht zäh, gelatinierbar, schwer fällbar	Koll. Kieselsäure[1]
6	nicht zäh, gelatinierbar, leicht fällbar	Benzopurpurin[2], Graham's Koll. Tonerde.
7	nicht zäh nicht gelatinierbar, schwer fällbar	Paal's koll. Metalle
8	nicht zäh nicht gelatinierbar, leicht fällbar	Schutz kolloidfreie Metalle, einige Sulfide, etc.

Aus folgendem Schema[3] (Tabelle II) ergibt sich, dass die Einteilung von Noyes nur zwei sehr weit voneinander entfernte Gruppen von Kolloiden näher charakterisiert. Die Mehrzahl derselben ist keiner der beiden Klassen einzuordnen.

TABELLE II

Umfang der Klasse I			Umfang der Klasse II
Beispiele: Gelatine Stärke und einige andere "Colloidal solutions"	Dextrin Caramel Thoriumoxyd Aluminiumoxyd Kongorot, etc.	Cassius'scher Purpur Zinnsäure Seifenlösungen Einige Sulfide Benzopurpurin, etc.	Beispiele: Reine Metallkolloide, einige Sulfide und Salze, etc. "Colloidal suspensions"

Auch Wo. Ostwald[4] ist bei dem Versuche, die Einteilung in "Suspensions" und "Emulsionskolloide" (bezw. "Suspensoide" und "Emulsoide") praktisch durchzuführen, schliesslich zu dem Resultate gelangt, dass sie unzweckmässig, "zuweilen sogar unmöglich" ist. Er schreibt darüber unter anderem:

"Sodann sind die speziellen Abteilungen[5] "Suspensoide" und "Emulsoide" weggefallen zugunsten der Rubrik "Spezielle experimentelle Kolloidchemie" aus der praktischen Erkenntnis heraus, dass in auserordentlich viel Fällen sich die Unterschiede zwischen diesen zwei Klassen Kolloider Lösungen verwischen."

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[1] Kieselsäure zeigt nur vor dem Gelatinieren eine beträchtliche (Zähigkeitszunahme).

[2] Gelatinierbar, zum Beispiel, bei der Dialyse.

[3] Das Schema und die Stellung der Beispiele in Tabelle I ändern sich etwas, wenn man die wörter zäh, gelatinierbar etc., anders auffasst als ich, aber immer werden sich zahlreiche Repräsentanten von Hydrosolen finden, welche in keiner der beiden Klassen von Noyes Platz haben.

[4] *Wo. Ostwald,* Koll. Z. 9. p. 29 (1911).

[5] In der Literaturübersicht der Kolloid-Zeitschrift (Anmerkung der Referenten. Z.)

Die Wo. Ostwald'sche Einteilung nach dem Aggregatzustande der zerteilten Materie würde brauchbar sein, wenn man ein Mittel hätte, den Aggregatzustand (Formart) der Ultramikronen festzustellen. Dies ist aber in weitaus den meisten Fällen unmöglich. Ausserdem zeight das Beispiel des kolloiden Quecksilbers,[1] dass das Verhalten der Hydrosole durch den Aggregatzustand der zerteilten Materie nicht wesentlich bestimmt wird, dass jedenfalls andere Faktoren als bloss der Aggregatzustand der zerteilten Materie dafür massgebend sind, ob ein gegebenes Kolloid sich wie ein lyophiles oder wie ein lyophobes verhält. Nach neueren Ausführungen von Wo. Ostwald[2] soll es hauptsächlich auf den komplexen Charakter des "Dispersoids" ankommen und der Aggregatzustand der dispersen Phase soll bei "Emulsoiden stetig variieren können zwischen vollkommen flüssig über zähflüssig zu fest, damit verlieren aber die Einteilung nach dem Aggregatzustand und ebenso die Wörter Suspensions—und Emulsionskolloide ihre Bedeutung.

Im folgenden will ich nun eine Einteilung besprechen, die jedenfalls den Vorzug hat bezüglich der bei gewöhnlicher Temperatur und Atmosphärendruck beständigen Kolloidlösungen[3] durchfuhrbar zu sein. Sie ist schon vor mehreren Jahren vorgeschlagen worden[4].

Man kann die Kolloide je nach ihrem Verhalten beim Eintrocknen in 2 Klassen einteilen. Zur ersten Klasse gehören kolloide, die einen Trockenrückstand hinterlassen, der im Dispersionsmittel wieder selbständig zum ursprunglichen Sol zerteilbar ist, zur zweiten Kolloide, denen diese Eigenschaft abgeht. Kolloide der ersten Klasse, zu denen Dextrin, Gummi arabicum, Eiweiss,

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[1] Physikalische Zeitschr. XI. p. 654 (1910).

[2] *Wo. Ostwald*, Grundriss der Kolloidchemie, 2 Aufl, p. 61 (1911).

[3] Es sind das wohl alle wichtigen Kolloidlösungen. Auf disperse Systeme, die nur bei sehr hohen orde sehr niedrigen Temperaturen oder bei extremen Drucken beständig sind, soll hier nicht eingegangen werden. Sie nehmen schon auf Grund ihrer Beständigkeitsbedingungen eine besondere Stellung ein und können auf Grund dieser in einer künftigen Einteilung den ihnezukommenden Platz angewiesen bekommen. Auch sind vorwiegend Hydrosole in Betracht gezogen, obgleich die Einteilung auch auf Organosole Anwendung finden kann.

[4] R. Zsigmondy, Zur Erkenntnis der Kolloide, Jena, 1905, Kap. II.

Gelatine, etc., gehören, wurden mit einem von Hardy[1] allerdings in anderem Sinne gebrauchten Ausdruck "*reversible* Kolloide" bezeichnet, Kolloide der zweiten Klasse mit dem Ausdruck *irreversible* Kolloide.

Um jedes Missverständnis auszuschliessen, dass es sich hier um die ursprüngliche Hardy'sche Einteilung handelt, deren Undurchführbarkeit schon früher nachgewiesen worden war,[2] sehe ich mich, trotzdem ich kein Freund der modernen Ueberschwemmung der Kolloidchemie mit neuen Wörtern bin, genötigt doch einen neuen Ausdruck einzuführen. Systeme der ersten Klasse seien daher als *resoluble* Kolloide, die der zweiten Klasse als *irresoluble* bezeichnet.

Die Durchführbarkeit dieser Einteilung ist ohne weiteres ersichtlich; man braucht nur das Kolloid bei Zimmertemperatur zur Trockne einzudampfen und zu prüfen, ob bei Berührung mit dem Dispersionsmittel das Sol mit seinen ursprünglichen Eigemschaften zurückgewonnen werden kann oder nicht.

Bei einigen der Kolloide ist dabei Temperaturerhöhung erforderlich, bei anderen nicht. Das gibt Veranlassung zu einer weiteren Einteilung:

Zur einen Gruppe der resolublen (reversiblen) Kolloide gehören Gelatine, Agar, Stärke, etc., zur anderen Dextrin, Gummi arab., Albumin, Graham's Molybdän und Wolframsäure, Lea's Silber, Paal's Gold.

Auch die irresolublen (irreversiblen) Kolloide lassen sich weiter einteilen:

Eine Gruppe von ihnen enthält Systeme, die schon während des Konzentrierens der kolloiden Lösung koagulieren und zwar so weitgehend, dass eine Peptisation des (meist pulvrigen) Niederschlags nicht mehr möglich ist, d.h. dass sie sich durch Hinzufügen kleiner Mengen von geeigneten Krystalloiden (Säuren, Alkalien, Salze) nicht mehr in das ursprüngliche Hydrosol zurückverwandeln lassen. Hierher gehören die schutzkolloidfreien kolloiden Metalle.

Die zweite Gruppe umfasst Kolloide, die sich weitgehend konzentrieren lassen, um bei erheblicher Konzentration zu koagulieren, wobei peptisierbare Gallerten entstehen (Zinnsäure, Kieselsäure, Eisenoxyd und Graham's Tonerde, etc.). Erst bei vollständigem Eintrocknen verliert sich meits die Peptisierbarkeit.

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[1] W. B. Hardy, Z. phys. Chem. *33*, p. 326-385 (1900).

[2] R. Zsigmondy, Zur Erk.d. Koll. p. 20.

Als Typus der ersten Gruppe kann das kolloide Gold, als Typus der zweiten die kolloide Zinnsäure angesehen werden.

Die kolloiden Sulfide stehen ungefähr in der Mitte zwischen diesen beiden Typen von Kolloiden, d.h. sie lassen sich je nach der Peptisierbarkeit des schon während des Eindampfens entstehenden Koagulums der einen oder der anderen Gruppe einordnen.

Das einfache Eindampfen und Wiederauflösen gibt demnach eine Reihe von Anhaltspunkten über die Natur des Kolloids und ermöglicht eine Einteilung in Gruppen, deren Glieder eine Anzahl charakteristischer Merkmale miteinander gemein haben. Die Einteilung ist unaghängig vom Dispersitätsgrad, d.h. in jeder einzelnen Gruppe können Glieder enthalten sein, die sowohl relativ grobe wie nahezu optisch homogene Zerteilungen enthalten.

Man könnte dieser Einteilung zum Vorwurf machen, dass sie die Temperatur des Eintrocknens und Wiederauflösens willkürlich auf Zimmertemperatur (15°–20° C.) festsetzt. Dieses Temperaturintervall ist aber das natürliche, durch unsere Arbeitsbedingungen von selbst gegebene: bei Zimmertemperatur operieren wir mit den Kolloidlösungen, bei Zimmertemperatur werden sie aufbewahrt, und wir sind fast immer genötigt, unsere Substanzen, wenn wir sie bei anderen Temperaturen beobachten wollen, einer künstlichen Temperatursteigerung oder—Erniedrigung auszusetzen.

Die Tabelle III gibt eine Uebersicht über die Einteilung.

TABLE III

EINTEILUNG NACH DEM VERHALTEN BEIM EINTROCKNEN

I. Resoluble Kolloide

(Die Kolloide lösen sich selbständig im Dispersionsmittel)

A. Zur Herstellung der kolloiden Lösung der bei Zimmertemperatur eingetrockneten Kolloide ist Temperaturerhöhung erforderlich[1]: Gelatine, Stärke, Agar-Agar, viele Seifen, etc.

B. Zur Herstellung der kolloiden Lösung ist *keine* Temperaturerhöhung erforderlich: Dextrin, Gummi arab., Paal's koll.

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[1] Der Zerteilungsgrad ist in auffälliger Weise von der Temperatur abhängig.

Metalle, überhaupt geschützte Metallkolloide, Graham's Wolfram und Molybdänsäure, Molybdänblau, Albumin, etc.

II. Irresoluble Kolloide

(Die Kolloide lassen einen unlöslichen Trockenrückstand zurück, da sie beim Eintrocknen irreversible Zustandsänderungen erleiden (darum auch *irreversible* Kolloide gennant).

A. Kolloide, die pulvrige, nicht mehr peptisierbare Niederschälge schon während des Eintrocknens geben: Reine Metallkolloide, einige Sulfide, Salze wie AgBr, AgCl, etc.

B. Kolloide, die beim Eintrocknen irreversible Zustandsanderungen erleiden und zunächst peptisierbare Gallerten geben: Zinnsäure, Kieselsäure, Eisenoxyd, Tonerde (Graham's).

Zur praktischen Durchführung dieser Einteilung muss allerdings das noch wenig bekannte Verhalten der einzelnen Kolloidlösungen beim Eintrocknen näher studiert werden. Auch macht sie erforderlich, dass Hydrosole, die gegenwärtig noch mit dem gleichen Namen bezeichnet werden, von einander getrennt werden. Ich habe daher in mienem Buche[1] "Kolloidchemie" die folgende Einteilung der Kolloidsysteme durchgeführt, die jedenfalls zünachst eine leichtere Orientierung gestattet als die oben näher erörterte:

I. Anorganische Kolloide
- A. Metalle:
    - 1. Reine Metallkolloide
    - 2. Metallkolloide mit Schutzkolloiden
- B. Andere Elemente (S, Se, etc.)
- C. Oxyde
- D. Sulfide
- E. Salze

II. Organische Kolloide
- A. Organische Salze:
    - 1. Seifen
    - 2. Farbstoffe
- B. Eiweisskörper:

Daran können andere Kolloide Z. B. Kohlehydrate angeschlossen werden.

---

[1] R. Zsigmondy, Kolloidchemie, Leipzig, 1912, Verl. Spamer.

Noch seien einige Werte über ein viel weiteres Gebiet, das der dispersen Systeme, dem die Kolloidlösungen selbst eingeordnet werden können, eingefügt. Will man die Gesamtheit der Zerteilungen (disperse Systeme) einteilen, so wird man sich mit grossem Vorteil an die Wo. Ostwald'sche Einteilung halten und die dispersen Systeme zunächst nach dem Aggregatzustand (Format) des Dispersionsmittels scheiden:

I. Disperse Systeme mit gasförmigem Dispersionmittel: Nebel (G+Fl), kosmischer Staub (G+F), etc.

II. Disperse Systeme mit flüssigem Dispersionsmittel: Gröbere Systeme: Suspensionen (Fl+F). Emulsionen (Fl+Fl): Feinere Systeme: hierher gehören die kolloiden Lösungen als feinere Zerteilungen ursprünglich fester Körper in Flüssigkeiten.

Ich halte es nicht für zweckmässig, diese selbst nach dem Aggregatzustand der zerteilten Materie (der meist unbekannt ist) einzuteilen[1], sondern zunächst nach den Bestandigkeitsbedingungen der dispersen Systeme: Solche die nur bei hoher Temperatur als flüssige Systeme beständig sind, Pyrosole (R. Lorenz): solche die bei gewöhnlicher Temperatur beständig sind, Sole Graham's oder kolloide Lösungen im engeren Sinne: solche, die nur bei tiefen Temperaturen beständig sind, einige Metallsole nach Svedberg, kolloides Eis (Wo. Ostwald, v. Weimarn), Kryosole.

Die weitere Einteilung erfolgt dann zweckmässig nach der Natur des Dispersionsmittels, also mit Graham in Hydrosole, Sulfosole, Alkosole, Aetherosole, etc. Diese letzteren könnten weiter nach ihrem Verhalten beim Eintrocknen in der oben geschilderten Weise klassifiziert werden.

Eine Fortführung der Einteilung könnte erzielt werden, wenn man die Natur der zerteilten Materie in Betracht zeiht (in Elemente, Oxyde, Sulfide, etc., organische Kolloide), oder, indem man die Sole in elektrolytähnliche und nichtelektrolytähnliche einteilte, oder endlich, indem man das Verhlten gegen einzelne *ganz bestimmte* Elektrolyte untersuchte und nach diesem enteilte (eine Klassifikation, ähnlich der in der analytischen Chemie üblichen).

---

[1] Diese Einteilung würde eine Unzahl von Spezial Hypothesen bezüglich des Aggregatzustandes (Format) der dispersen Phase erforderlich machen und Streitfragen über den Aggregatzustand heraufbeschwören.

III. Disperse Systeme mit *festem* Dispersionsmittel könnten eingeteilt werden zunächst etwa in Systeme mit krystallisiertem und mit amorphem Dispersionsmittel.

Die modificierte Ostwald'sche Einteilung der dispersen Systeme würde sich ungefähr folgendermassen gestalten (Tabelle IV).

TABELLE IV

EINTEILUNG DER DISPERSEN SYSTEME

I. Disperse Systeme mit gasformigem Dispersionsmittel

A. Grob disperse Systeme:

(a) G+Fl: Regen, Nebel

(b) G+F: vulkanischer Aschenregen, vulkanischer Staub in der Atmosphäre, nuée ardente.

B. Fein disperse Systeme:

Atmosphäre mit kleinen Teilchen, die nach Lord Rayleigh am Zustandekommen des Himmelsblau beteiligt sind; Metallzerstäubungen (Ehrenhaft).

II. Disperse Systeme mit flüssigem Dispersionsmittel

A. Grob disperse Systeme: Teilchengrösse bis zu 0,1 u herab

(a) Fl+F: Suspensionen:

(b) Fl+Fl: Emulsionen.

B. Fein disperse: Systeme: Teilchengrösse zwischen etwa 0,1 und 0,001 u—

(a) Pyrosole: Metallnebel in geschmolzenen Salzen

(b) Kolloide Lösungen im engeren Sinne

mit anorganischem Dispersionsmittel:

1. Hydrosole
    1. Resoluble Hyrdosole vom Dextrintypus—vom Gelatinetypus
    2. Irresoluble Hydrosole vom Typus der Zinnsäure—vom Typus des Goldes
2. Sulfosole u. andere.

mit organischem Dispersionsmittel (Organosole)

z.B. Alkosole, Aethersole, Acetosole, etc.

c)Kryosole: Einige Koll. Metalle (Svedberg), koll. Eis (v. Weimarn, Wo. Ostwald).

III. Disperse Systeme mit festem Dispersionsmittel

- A. Grob disperse Systeme:
    - (a) F+F: Gesteinsarten (erstarrte Pyrosole, Silikate):
    - (b) F+Fl: Mineralien mit flüssigen Einschlüssen:
    - (c) F+G: Mineralien mit gasförmigen Einschlüssen.
- B. Fein disperse Systeme:
    - (a) Zerteilungen in krystallisierten Substanzen (Gefärbtes Steinsalz, Rubine, Mondstein, etc.)
    - (b) Zerteilungen in amorphen Substanzen (Rubingläser, Opale, etc.)

Die Einteilung könnte noch beträchtliche Erweiterung erfahren, wenn man die Klassen I und III, nach Beständigkeitsbedingungen etc., einteilte, ähnlich wie Klasse II. Vorläufig ist eine solche Erweiterung nicht erforderlich.

In voliegender Abhandlung musste ich mich aus sachlichen Gründen gegen die Einteilung von Noyes aussprechen. Meine Einwände richten sich aber nicht gegen die sonstigen Ausführungen dieses Forschers, der den Gegenstand im übrigen in vorzüglicher Weise und mit grossem Scharfsinn beurteilt hat. Vor allem sollen die ausgeseichten Worte, die Noyes im Anschluss an die Besprechung der Koagulation bezüglich einer modernen Richtung in der Kolloidliteratur zum Ausdruck brachte, hier wiederholt werden. Seine Worte verdienten nicht nur so oft wie möglich abgedruckt zu werden, sie sollten in alle Sprachen übersetzt werden.

Noyes[1] schreibt bezüglich der Erklärungsversuche betreffs des Mechanismus der Koagulation:

"Interesting though they are, I shall not try to describe the explanations that have been suggested, for, in my opinion, mere speculative hypotheses, that is, hypotheses which have not been shown to facilitate to an important extent a knowledge of the actual phenomena, are of little value except to the investigators of them and to them only because of the possibility of their future development into really useful conceptions. The recent

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[1] Arthur A. Noyes, Journ. of Amer. Chem. Soc. *27*, p. 103 (1905).
Göttingen, Institut für anorganische Chemie.

literature of colloids furnishes a striking example of the unfortunate tendency even of our modern investigators and text-book writers to attach greater importance to hypothetical interpretations of imperfectly known phenomena than to a determination and presentation of the laws in regard to them."

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